GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA
April 13, 1959

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 1, Project No. A-421
Photochemically Induced Diels-Alder Reactions
Georgia Tech Research Institute
January 2, 1959 - March 31, 1959
OOR Project No. 2123C, Contract No. DA-01-009-ORD-709

Gentlemen:

Work was begun for the present quarter upon the structure of the photochemically produced adduct from benzene and maleic anhydride. The previous work* from our laboratory showed that the adduct consisted of one molecule of benzene combined with two molecules of maleic anhydride. The chemical properties of the adduct and its infrared, ultraviolet and nuclear magnetic resonance spectra are in agreement with the structure (I). What appears to be needed for confirmation is degradation of the adduct to known reference compounds.

Possible degradation routes are shown in Figure 1. In Scheme 1 the adduct (I) is converted to the tetra-hydrazide (II) which is degraded to the tetra-amine (IV) via the Curtius reaction. Because acids which readily form five-membered cyclic anhydride rings frequently give cyclic secondary hydrazides (thus see V) and since the latter do not undergo the Curtius reaction, Scheme 2 is simultaneously under consideration. In Scheme 2 the secondary hydrazide V is oxidized to the azo compound VI which possibly simultaneously loses nitrogen and carbon monoxide to give the olefin VII. As far as we are aware a reaction of the type of V to VII has never been reported but appears to represent an attractive possibility.

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*James W. Taylor, M. S. Thesis, Georgia Institute of Technology, June 1958.

The tetramethyl ester of adduct I has been found to react with hydrazine under mild conditions to give a product (A) whose nitrogen content agrees with that expected for a dihydrazide-dimethyl ester of I. Vacuum sublimation of (A) removes hydrazine and converts (A) into a substance (B) whose nitrogen content agrees with that expected for a dimethyl ester of a cyclic secondary hydrazide of I. Treatment of (B) with hydrazine under mild conditions regenerates (A). Evidently two of the carboxyls of adduct I combine more readily with hydrazine than the remaining two carboxyls. While Schemes 1 and 2 could, possibly advantageously, be carried out stepwise via dihydrazide (A) and secondary hydrazide (B), efforts are underway to make the full hydrazides II and/or V. In the latter regard, the direct reaction of the anhydride (I) with hydrazine is under investigation.

While Schemes 1 and 2 represent reasonably attractive modes for degradation of the adduct, recently it has come to our attention that cis-1,2-dicarboxylic acids may be oxidized with lead tetraacetate* to give fair to good yield of olefin as shown for our adduct in Scheme 3. We therefore hope to initiate such oxidation studies upon the acid VIII of adduct I in the near future.

cis-Cyclohexane-1,2-dicarboxylic anhydride is readily available and will be used as a model compound for reactions to be studied on adduct I in the future.

Respectfully submitted,

Erling Grovenstein, Jr.

D. V. Rao

Approved:

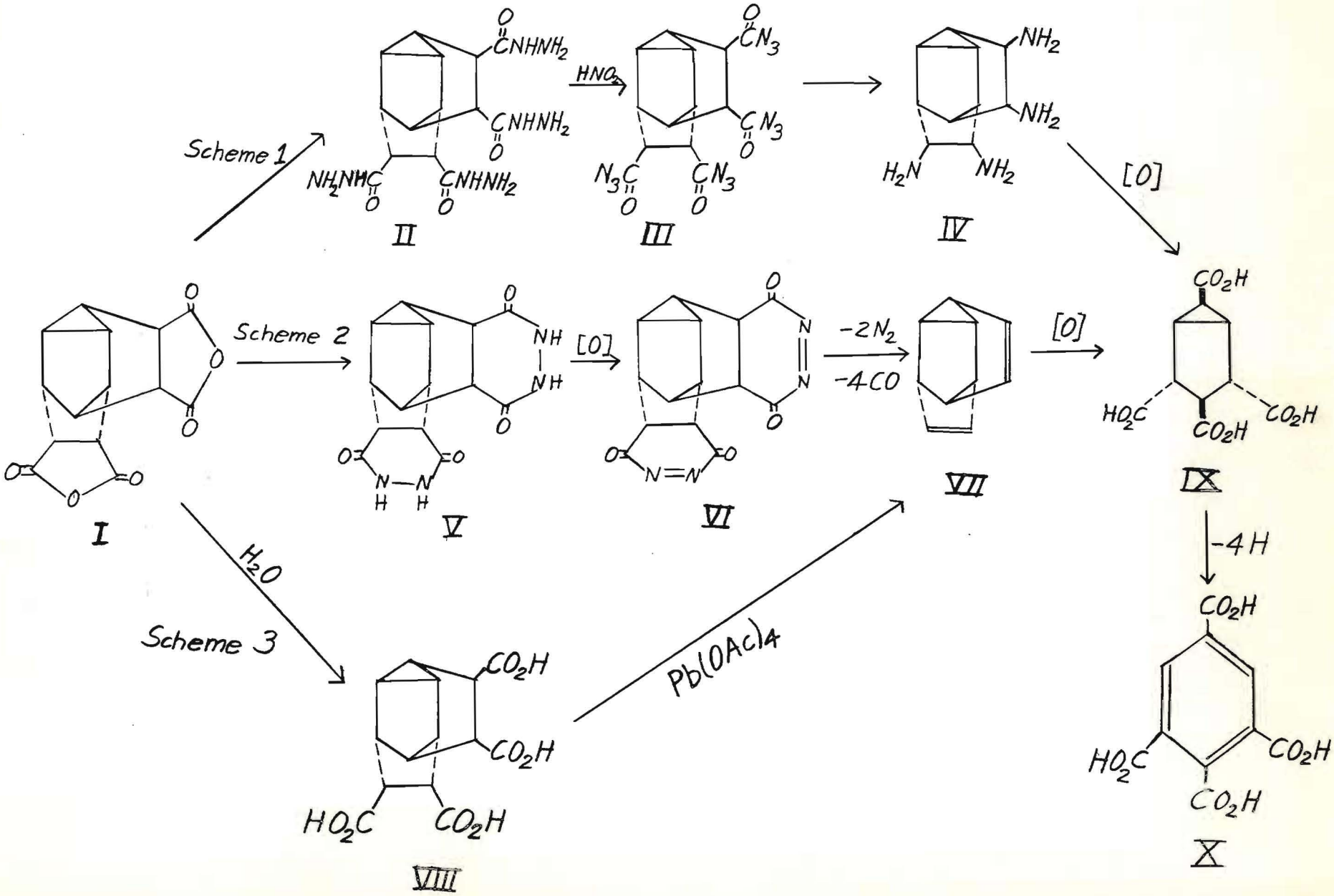
Wyatt C. Whitley, Chief
Chemical Sciences Division

*C. A. Grob, M. Ohta, and A. Weiss, Angew. Chem., 70, 343 (1958).

Figure 1

Schemes for Degradation of the Adduct from

Benzene and Maleic Anhydride



A-421

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

July 1, 1959

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 2, Project No. A-421
Photochemically Induced Diels-Alder Reactions
Georgia Tech Research Institute
April 1, 1959 - June 30, 1959
OOR Project No. 2123C, Contract No. DA-01-009-ORD-709

Gentlemen:

During the past quarter work was begun on the preparation of derivatives of cis-cyclohexane-1, 2-dicarboxylic anhydride (I) for use as model compounds in study of the chemical and physical properties of the adduct (II) from the photochemically induced reaction between benzene and maleic anhydride. Toward this end I was esterified with methanolic hydrogen chloride to give dimethyl cis-cyclohexane-1,2-dicarboxylate (III). This ester has an absorption maximum at 213 mμ (ϵ, 140) while the tetramethyl ester of II has a maximum at 214 mμ (ϵ, 1020). These esters absorb at essentially the same wavelength as expected for the structure tentatively proposed for II (see Status Report No. 1); however the extinction coefficient of the tetramethyl ester is higher than expected by analogy with that of III. Compound III reacted in good yield with methanolic hydrazine to give the corresponding dihydrazide, whose properties were in reasonable agreement with those described in the literature. The dihydrazide sublimed with little decomposition at 0.015 mm; however, at 23 mm. this substance distills with evident loss of hydrazine to give a product of m.p. 52-55°. Recrystallization gave a compound of m.p. 124-125.5°, which has been submitted for elementary analysis. This compound is tentatively regarded as the previously unknown cyclic secondary hydrazide of I.

A photochemically induced reaction between naphthalene and maleic anhydride in acetone has been attempted. After irradiation for 17.4 hours, however, 97.8% of the napthalene used could be recovered unchanged. About 2.5% of the maleic anhydride was isolated after irradiation as fumaric acid. It appears, therefore, that little if any photochemically induced reaction occurred between naphthalene and maleic anhydride under the conditions investigated.

Maleic anhydride (10 g.) dissolved in thiophene and irradiated for 18 hours with ultraviolet light gave some 0.3 g. of a dark brown material on the walls of the irradiation cell. This material contained sulfur but did not dissolve

appreciably in aqueous KOH or acetone. From the thiophene layer, after extraction with water to remove maleic anhydride and distillation to remove thiophene, there was obtained some 0.2 g. of a dark brown residue. This material gave a strong positive test for sulfur upon sodium fusion and much of the product could be distilled in vacuo. The resulting red-black tarry distillate was insoluble in water but readily soluble in aqueous KOH and in acetone. Evidently, therefore, some reaction occurred between maleic anhydride and thiophene.

Yours very truly,

Erling Grovenstein, Jr.
Project Director

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

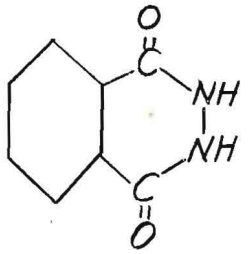
October 1, 1959

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

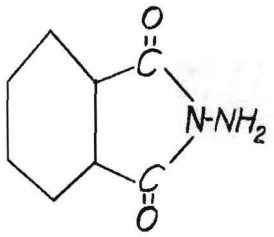
Subject: Status Report No. 3, Project No. A-421
Photochemically Induced Diels-Alder Reactions
Georgia Tech Research Institute
July 1, 1959 -- September 30, 1959
OOR Project No. 2123 C, Contract No. DA-01-009-ORD-709

Gentlemen:

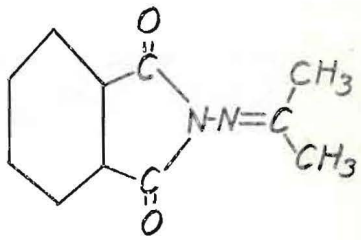
We reported* that the dihydrazide of cis-cyclohexane-1,2-dicarboxylic acid (I) upon distillation at 23 mm. gives a compound (II) of m.p. 52-55° and that the latter compound upon recrystallization from acetone gave a compound (III) of m.p. 124-125.5°. We tentatively regarded the higher melting product as the cyclic secondary hydrazide of (I). We now find that the compound (II) of m.p. 52-55° upon three distillations in vacuo has m.p. 60-62.5° and has an elementary analysis (C, H, and N) which agrees with the formula $C_8H_{12}O_2N_2$ as expected for the cyclic secondary hydrazide of (I). On the other hand, the higher-melting product III from recrystallization of this hydrazide from acetone has analyses in fair agreement with $C_{11}H_{16}O_2N_2$. The hydrazide $C_8H_{12}O_2N_2$ has structure A or B while structure C appears to be the only probable structure for the compound $C_{11}H_{16}O_2N_2$. The formation of (C) from



A



B



C

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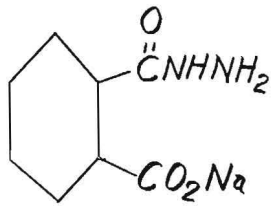
* Status Report No. 2 from our laboratory

recrystallization of compound II from acetone does not necessarily prove that II has structure B since structures of type A are known to give such derivatives under some conditions.* Compound II titrates as a monobasic acid as expected for structure A on the basis of a recent report** for cyclic succinhydrazide; however, our data indicates that under the conditions of the titration II undergoes hydrolytic cleavage to (D). Since both structures A and



D

B might be expected to hydrolyze readily to give D, this titration is not diagnostic of structure. We conclude that compound II probably has structure A, since in view of the high temperature used in the preparation of II (280-290°) the more stable isomer should be produced and structure A is expected to be more stable than B because of less steric strain and a higher resonance energy.

Solutions of 10.0 g. of maleic anhydride in 300 to 330 ml. of chlorobenzene, toluene, or p-xylene have been irradiated with ultraviolet light for 20 to 23 hours. The yields of crude product from these reactions were respectively 1.0, 8.2, and 10.0 g. These yields are to be compared with some two grams of product obtained with benzene under similar conditions. The yields of product are seen to parallel the expected stability of the molecular complexes*** formed by benzenoid compounds with dienophiles (here maleic anhydride).

The product from chlorobenzene has not been isolated in a pure state but has been found to contain chlorine and to be soluble in aqueous KOH, but insoluble in water or hydrochloric acid. This product, therefore, evidently consists of chlorobenzene combined with maleic anhydride.

The product from toluene has been isolated in part as an acid of m.p. 162-163° which gave a satisfactory C,H-analysis for $C_{11}H_{12}O_4$ and, therefore, appears to consist of one mole of toluene combined with one mole of maleic acid.

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* H. D. Drew and H. H. Hatt, J. Chem. Soc., 16 (1937).
** H. Feuer, G. B. Bachman, and E. H. White, J. Am. Chem. Soc., 73, 4716 (1951).
*** R. E. Merrifield and W. D. Phillips, J. Am. Chem. Soc., 80, 2778 (1958).

The remainder of the product from this reaction was an oil which was esterified with methyl alcohol. The resulting methyl ester could be distilled at 0.015 mm at a bath temperature of 145°. After two distillations *in vacuo* the ester was a pale yellow oil which had a satisfactory C,H-analysis for $C_{13}H_{16}O_4$ and therefore appears to consist of one mole of toluene combined with one mole of dimethyl maleate. Gas chromotography of the methyl ester on a fire-brick packing impregnated with silicone oil at 247 or 288° gave two strong, two medium, and four rather weak bands. Evidently the methyl ester consists of a complex mixture of compounds although at the temperature of the chromatogram some thermal isomerisation may be taking place.

The product from *p*-xylene has been isolated in part (1.1 g.) as a crystalline substance of m.p. 86-87°. This material was vacuum sublimed at a bath temperature of 95-100° at a pressure of 0.02 mm. The substance had a satisfactory C,H-analysis for $C_{12}H_{12}O_3$ as expected for an adduct of one mole of *p*-xylene combined with one mole of maleic anhydride. The major portion of the product was an oil or sticky solid whose composition is under investigation.

Irradiation of 20 ml. of dimethyl acetylenedicaroboxylate in 300 ml. of benzene with ultraviolet light for 24 hours gave 4.1 g. of a tarry product. Most of the product dissolved in ether and left behind a brown solid (0.4 g.). The ether-soluble product could be largely distilled at a bath temperature of 140° at 0.015 mm. After three distillations *in vacuo* the product was an oil with a light orange-yellow color. This substance did not have a C,H-analysis in agreement with any simple combination of benzene with dimethyl acetylene dicarboxylate; however, the analysis was fairly close to that expected for a one-to-one adduct.

Yours very truly,

Erling Grovenstein, Jr.
Project Director

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

A-421

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

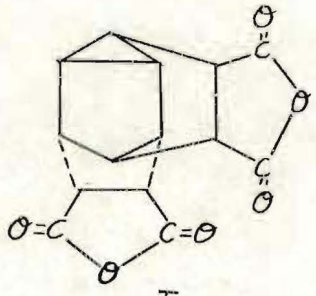
January 2, 1960

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

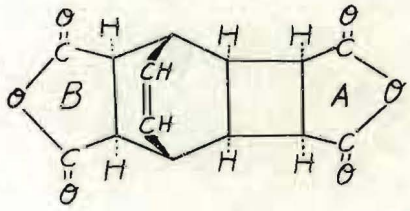
Subject: Status Report No. 4, Project No. A-421
Photochemically Induced Diels-Alder Reactions
Georgia Tech Research Institute
October 1, 1959 - December 31, 1959
OOR Project No. 2123C, Contract No. DA-01-009-ORD-709

Gentlemen:

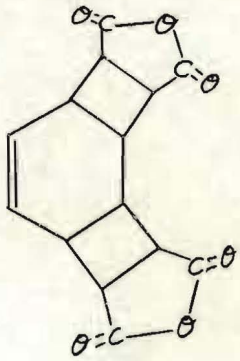
Three structures which are in accord with the principle of minimum structural change for the adduct produced photochemically from maleic anhydride and benzene are I, II and III:



I



II



III

Our early work[1] suggested structure I for the adduct. While the tetracarboxylic acid of the adduct slowly absorbed about one molar equivalent of hydrogen over a 24 hour period when hydrogenated at one atmosphere over a 5% Pt on C catalyst, the anhydride and the corresponding tetramethyl ester failed to react appreciably with bromine or $KMnO_4$ under the usual conditions for tests for unsaturation. We, therefore, favored structure I. Recent work, however, has shown that the tetrasodium salt of our adduct reacts rapidly with bromine in water (although the tetracarboxylic acid in aqueous HCl reacts only slowly) and, moreover, reacts in 72 hours at room temperature with 9.7% or at 50° with 70% of one mole of iodine per mole of sodium salt.

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[1] J. W. Taylor, M. S. Thesis, Georgia Institute of Technology, June, 1958.

For comparison, $C_6H_5CH = CHCH_2CO_2Na$ is 100% reacted and $C_6H_5CH(CO_2Na)CH = CH_2$ is 23% reacted with I_2-KI in water at 25° in one hour's time. In these reactions halo-lactones are doubtlessly formed, and, therefore, the adduct appears to have an ethylenic bond. Angus and Bryce-Smith[2], who have recently independently discovered the photochemically induced reaction between benzene and maleic anhydride, have found that the tetramethyl ester of the adduct by per-acid titration gives one double bond per molecule. Finally, the nuclear magnetic resonance absorption spectrum[1] of the tetramethyl ester has been reinterpreted[3] in light of recently published data[4,5] and shows the presence of an ethylenic bond (although the ethylenic proton chemical shift occurs in the region recorded for tiglaldelyde or benzene rather than for cyclohexene) and the absence of absorption in the region expected for hydrogen attached to a cyclopropane ring. Structure I is therefore excluded. Structure III is improbable because it locates the two maleic anhydride moieties in equivalent positions while, as judged by the behavior[6] of the tetramethyl ester with hydrazine, two of the carbomethoxyl groups are considerably more readily attacked by hydrazine than the other two and these reactive carbomethoxyl groups must be attached to the same maleic acid moiety since the dihydrizide may be pyrolyzed to a cyclic hydrazide. We are left with structure II as the most probable structure of the adduct. We believe that the adduct has the detailed stereochemical structure shown (see page 1) with both maleic anhydride moieties fused <u>endo</u> to the olefinic bond. Models show that the maleic anhydride moiety A would highly hinder the approach of external reagents to its side of the double bond. Such geometry accounts for the unreactivity of the adduct or its methyl ester toward a reagent such as bromine, which normally adds <u>trans</u> to an olefinic bond. On the other hand, bromine and iodine readily attack the sodium salt of II, doubtlessly, because of participation of a neighboring carboxylate group to give a halo-lactone. The decreased reactivity of II and derivatives toward reagents such as $KMnO_4$ and hydrogen, which normally add <u>cis</u> to olefinic bonds, is attributed to some steric hindrance as well from maleic anhydride moiety B. This hindrance, however, appears to be small compared to that exerted by A.[7]

The acid of m.p. 162-163 reported previously[8] from irradiation with ultraviolet light of a solution of maleic acid in toluene is now identified as benzylsuccinic acid. According to separations by crystallization and chromatography on silica gel, this acid constitutes some 78% of the reaction

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[2] H. J. F. Angus and D. Bryce-Smith, <u>Proceedings of the Chemical Society</u>, 326 (1959).

[3] We are indebted to Dr. James D. Ray for aid in this interpretation.

[4] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, p. 236.

[5] E. F. Ullman, <u>Chemistry and Industry</u>, 1173 (1958).

[6] Status Report No. 1.

[7] We are writing up a report of this portion of our work for publication.

[8] Status Report No. 3.

product. The remainder of the product is not identified but is of considerable interest. The peroxide catalyzed addition of toluene to maleic anhydride is reported[9] to give benzylsuccinic acid and it is stated that such reactions are catalyzed by ultraviolet light, but no details of the light catalyzed reaction are given. The reaction which gives benzylsuccinic acid appears to proceed via a free radical process; therefore, we have attempted to prevent this reaction by addition of inhibitors. Irradiation of 10.0 g of maleic anhydride in 275 ml. of toluene containing 50 ml. of acetone and 1.0 g. of hydroquinone for 24 hours, with nitrogen bubbling through the solution, gave 1.39 g. of product (compared to 8.2 g. formed[8] in absence of the inhibitor). This product (after hydrolysis) contains at least 40% benzylsuccinic acid according to a separation by recrystallization from chloroform.

The crystalline anhydride of m.p. 86-87° which was reported[8] from irradiation of a p-xylene solution of maleic anhydride upon hydrolysis gives an acid of m.p. 115-117.5°. This acid appears to be p-methylbenzylsuccinic acid (m.p. 114-115°) which has been prepared[9,10] by a peroxide catalyzed addition of p-xylene to maleic anhydride at 100 - 150°. The thick oily liquid from which the anhydride was separated by crystallization upon esterification with methanol, distillation, saponification, and crystallization was found to contain at least 43% p-methylbenzylsuccinic acid. Therefore this acid (or its anhydride) constitutes at least 50% of the product of reaction of p-xylene with maleic anhydride under our conditions.

Yours very truly,

Erling Grovenstein, Jr.
Project Director

Approved:

W. C. Whitley, Chief
Chemical Sciences Division

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[9] W. G. Bickford, G. S. Fischer, F. G. Dollear, and C. E. Swift, Journal American Oil Chemists' Soc., 25, 251 (1948).

[10] H. Shechter and H. C. Barker, Journal Organic Chemistry, 21, 1473 (1956).

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

April 11, 1960

Commanding Officer
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2127 Myrtle Drive
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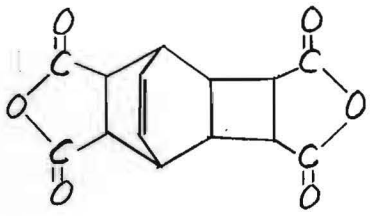
Durham, North Carolina

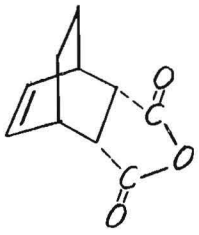
Subject: Status Report No. 5, Project No. A-421
Photochemically Induced Diels-Alder Reactions
Georgia Tech Research Institute
January 1, 1960 - March 31, 1960
OOR Project No. 2123C, Contract No. DA-01-009-ORD-709

Gentlemen:

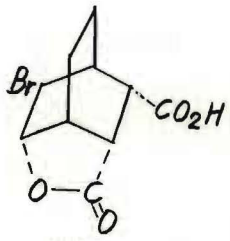
The structure of the adduct (I) produced photochemically from maleic anhydride and benzene is being investigated. The tetrasodium salt of the adduct reacts rapidly[1] with one molar equivalent of bromine in water. From this reaction a carboxylic acid has been isolated and this acid reacted with excess diazomethane to give a methyl ester, m.p. 215.0-216.3° which had satisfactory C, H, and Br analyses for $C_{17}H_{19}BrO_8$. This product, therefore, is a trimethyl ester of a bromolactone of (I). This bromolactone has absorption at 5.63 and 5.80 microns. Bellamy[2] states that gamma-lactones absorb at 5.62 - 5.68 microns, delta-lactones at 5.71 - 5.76 microns, and normal saturated esters at 5.72 - 5.76 microns. Our bromolactone would, therefore, appear to be a gamma-lactone. For purposes of comparison, the methyl ester of the known[3] bromolactone III of the adduct II was prepared and found to



I
Provisional Structure



II



III

[1] Status Report No. 4

[2] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, 1954, p. 153.

[3] K. Alder and G. Stein, Ann., 514, 1(1934).

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absorb at 5.69 and 5.79 microns. These values are in only fair agreement with Bellamy's values for a gamma-lactone ester and raise the question of whether the application of Bellamy's values to polycyclic compounds is justified for distinction of gamma- from delta-lactones.

As noted previously the sodium salt of the tetracarboxylic acid of adduct I reacts very slowly with I_2-KI solution at room temperature; for example, it gives only 9.8% reaction in 72 hours. In contrast, the sodium salt of the cyclohexadiene-maleic anhydride adduct II gives 97.5% reaction under similar conditions in 23.5 seconds. Thus iodolactone formation occurs about a million times faster with the sodium salt of II than with the salt of I. These results suggest that the double bond of I is sterically hindered. Similarly while the sodium salt of I decolorizes aqueous $KMnO_4$ very slowly (giving some apparent decoloration within a half hour), the sodium salt of II immediately decolorizes aqueous $KMnO_4$.

The sodium salt of I shows no absorption maxima down to 210 mμ but does show "end-absorption" (ϵ at 240 mμ $\simeq$ 50 and at 210 mμ $\simeq$ 2200). The sodium salt of II likewise shows no absorption maxima in the near ultraviolet but has "end-absorption" (ϵ at 240 mμ $\simeq$ 10 and at 210 mμ $\simeq$ 1650). Our previously reported absorption maxima for derivatives of I are now found to be erroneous and arose from light scattering, which can be significant at low intensities of light produced by absorption by the solvent.

The oxidation of cis-cyclohexane-1,2-dicarboxylic acid to cyclohexene with lead tetraacetate has been found to proceed satisfactorily in benzene solution after the method of Grob[4] and co-workers. Application of this procedure to degredation of the benzene-maleic anhydride adduct (I) or the corresponding tetracarboxylic acid is made difficult by the insolubility of either of these compounds in benzene. Since the tetramethyl ester of I is soluble in benzene, it seemed possible that some of the partial methyl esters of I would be soluble in benzene.

For preparation of partial methyl esters the tetramethyl ester of I (5.0 g.) was refluxed for one hour with two molar equivalents of KOH in methanol. From the reaction mixture after removal of methanol and acidification there was obtained 0.5 g. of crystalline material and 3.7 g. of viscous liquid. These were separated on the basis of the greater solubility of the liquid fraction in benzene. The crystalline fraction after two recrystallizations from acetone-benzene had m.p. 268-269° and had a C, H-analysis in fair agreement with that expected for a dimethyl ester, $C_{16}H_{18}O_8$. Lead tetraacetate oxidations of these partial methyl esters of I are now in progress.

Yours very truly,

Erling Grovenstein, Jr.
Project Director

Approved:

W. C. Whitley, Chief
Chemical Sciences Division

[4] C. A. Grob, M. Ohta, and A. Weiss, Angew. Chem., 70, 343(1958).

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

July 11, 1960

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
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Durham, North Carolina

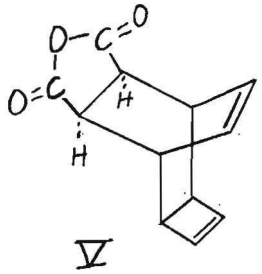
Subject: Status Report No. 6, Project No. A-421
Photochemically Induced Diels-Alder Reactions
Georgia Tech Research Institute
April 1, 1960 - June 30, 1960
OOR Project No. 2123C, Contract No. DA-01-009-ORD-709

Gentlemen:

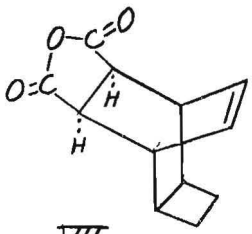
The structure of the adduct (I) produced photochemically from maleic anhydride and benzene has been under intensive investigation. Our most important discovery during the period of the present report is that lead tetraacetate oxidation of the tetracarboxylic acid of the adduct (I) in pyridine solution gives a crystalline product which is identical with the maleic anhydride addition product of cyclooctatetraene. This discovery along with previously available information permits us to arrive at both a structural and a probable stereochemical formula for the adduct (I). For a summary of all the work to date see the attachment, which is a copy of a communication which has been submitted for publication in the Journal of the American Chemical Society.

We have obtained some additional data concerning the stereochemistry of the maleic anhydride adduct (V) of cyclooctatetraene. Cope and co-workers (J. Am. Chem. Soc. 74, 4867 (1952)) noted that this adduct undergoes catalytic hydrogenation most readily at the double bond in the 4-membered ring to give VII and they, therefore, pointed out that Reppe's bromolactonic acid might also involve reaction of bromine with the double bond in the 4-membered ring rather than the 6-membered ring as Reppe had formulated it. As some confirmation of this opinion Cope and co-workers stated that VII "does not react readily with bromine," but gave no details of their reaction conditions. We find that the potassium salt of VII in water almost instantaneously consumes one molar equivalent of bromine to give a crystalline product which has satisfactory C, H, and Br analyses for VIII. The crystalline methyl ester of VIII also has satisfactory C, H, and Br analyses and has infrared absorption in the carbonyl region at 5.65 and 5.77 μ. We find that the methyl ester of the bromolactone of V has absorption at 5.69 and 5.76 μ. These compounds, therefore, appear to be gamma-lactones. From these data the steric location of the carboxyl groups in V relative to the double

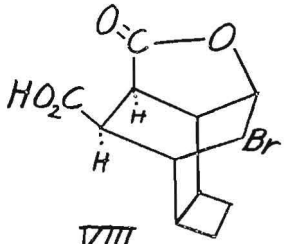
bonds is confirmed to be as shown below.



V



VII



VIII

Yours very truly,

Erling Grovenstein, Jr.
Project Director

Approved:

W. C. Whitley, Chief
Chemical Sciences Division

Attachment

Photochemical Adduct from Benzene and Maleic Anhydride[1]

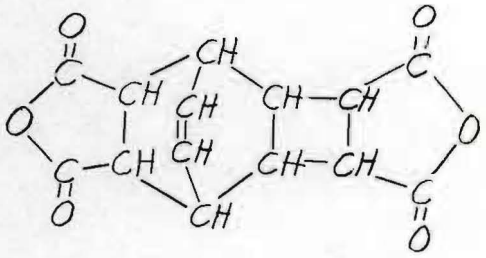
(1) Supported in part by the Office of Ordnance Research, U. S. Army.

Sir:

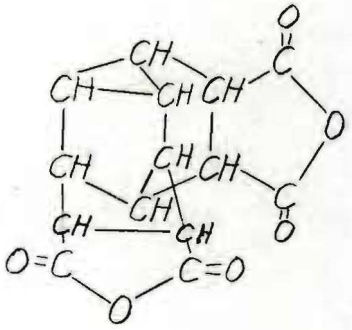
Angus and Bryce-Smith in a recent communication[2] have described the addition

(2) H. J. F. Angus and D. Bryce-Smith, Proc. Chem. Soc. (London), 326 (1959).

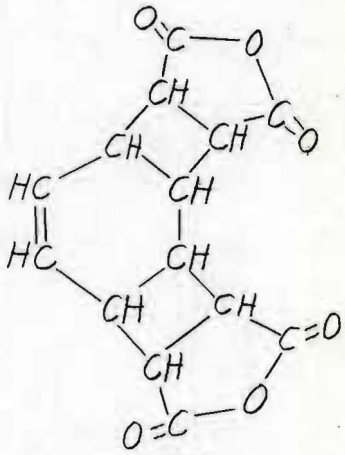
of maleic anhydride to benzene at 60° under the influence of ultraviolet radiation to give a product which they provisionally suggest has the structure (I). We wish to describe our work[3] upon this adduct. Irradiation with ultraviolet



(I)



(II)



(III)

(3) In part from the M. S. thesis of J. W. Taylor, Georgia Institute of Technology, June, 1958. Our discovery of the 2:1 adduct of maleic anhydride and benzene was announced by E. G. at the Seventh Reaction Mechanisms Conference, University of Chicago, September 5, 1958, during the discussion of the paper of Prof. G. Büchi on light-catalyzed organic reactions.

light of a nearly saturated solution of maleic anhydride in benzene at room temperature for 16 hrs. in an apparatus previously described[4] gave some 13%

(4) E. Grovenstein, Jr., and S. P. Theophilou, This Journal, 77, 3795 (1955).

yield (based on maleic anhydride) of product of m.p. 355-357° (dec.) The product analyses for $C_{14}H_{10}O_6$ [found: C, 61.24; H, 3.64] and has a saponification equivalent

of 68.4 as expected for an adduct from 1 mol. benzene combined with 2 mol. maleic anhydride. The adduct is somewhat soluble in acetone but is essentially insoluble in common organic solvents such as benzene and ether. The adduct can be sublimed at 240° and 0.02 mm pressure with slight decomposition. The adduct yields, upon refluxing with 0.08 N methanolic hydrogen chloride, a tetramethyl ester, m.p. 134.5-135.0° [found: C, 58.91; H, 5.89; mol. wt. in camphor, 366]. The methyl ester when heated at reflux for 4 hours in methanol containing a large excess of hydrazine gave a 90% yield of a dihydrazide, $C_{16}H_{22}O_6N_4$, m.p. 234° [found: C, 51.8; H, 6.01; N, 15.36]. The dihydrazide when distilled at 0.01 mm. lost hydrazine and gave a cyclic hydrazide, $C_{16}H_{18}O_6N_2$, m.p. 206.5° [found: C, 57.65; H, 5.55; N, 8.32]. The cyclic hydrazide when heated at reflux for 1.5 hours in methanol containing a large excess of hydrazine deposited crystals (88% yield) of the starting dihydrazide.

The tetracarboxylic acid from saponification of the adduct decomposed with loss of water at 125-200° and finally melted as the anhydride. The acid upon hydrogenation in glacial acetic acid over a 5% Pt on C catalyst at room temperature and atmospheric pressure slowly absorbed over a 24-hour period 0.925 mole of hydrogen per mole of acid. The anhydride did not decolorize $KMnO_4$ in acetone and showed no reaction with bromine in boiling acetic acid under otherwise the usual conditions for these tests. Similarly, the methyl ester did not decolorize $KMnO_4$ in ethanol nor show any reaction with bromine in methanol in the dark, the latter even after 6 days. We were led on the basis of these observations to postulate[3] the presence of a cyclopropane ring in our adduct as in structure II, which could be formed by 1,4-addition of one molecule of maleic anhydride to benzene and 1,5-addition[5] of a second molecule of anhydride.

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(5) Cf. the thermal addition of maleic anhydride to bicyclo[2:2:1]-heptadiene, E. F. Ullman, Chem. & Ind. (London), 1173 (1958).

However while the sodium salt of the tetracarboxylic acid does not decolorize $KMnO_4$ appreciably in 5 minutes, some decolorization occurs within a half hour. Similarly the tetracarboxylic acid in dilute hydrochloric acid solution slowly decolorizes bromine-water over a period of several hours. In sharp contrast, the sodium salt of the tetracarboxylic acid in aqueous solution reacts almost instantaneously with bromine to give a bromolactone which gave with diazomethane a trimethyl ester, $C_{17}H_{19}BrO_8$, m.p. 215-216° [found: C, 47.15; H, 4.38; Br, 18.55]. This ester has infrared absorption at 5.63 and 5.80 μ as

expected respectively for the carbonyl group of a gamma-lactone and of a carbomethoxyl group. Moreover the sodium salt of the tetracarboxylic acid with I_2-KI solution absorbs in 72 hours at room temperature 9.8% or at 50° 70% of one mole of iodine per mole of acid. In comparative runs under similar conditions the sodium salt of endo-cis-bicyclo[2,2,2,]-5-octene-2,3-dicarboxylic acid[6] (IV) immediately decolorizes aqueous $KMnO_4$ and absorbs 97% of one molar equivalent of

(6) K. Alder and G. Stein, Ann., 514, 15 (1934).

iodine in 23 seconds at room temperature (i.e., iodination occurs about a million times faster with the salt of IV than with the salt of the benzene-maleic anhydride adduct). Angus and Bryce-Smith[2] report that per-acid titration of the tetramethyl ester of the benzene adduct indicates the presence of one ethylenic bond.

The sodium salt of the tetracarboxylic acid shows no ultraviolet absorption maxima down to 210 mμ but does show "end-absorption"; the ultraviolet absorption spectrum of the sodium salt of IV is similar to that of the tetracarboxylic acid. Angus and Bryce-Smith[2] report for the tetracarboxylic acid (?) a weak absorption maximum at 265 mμ.

The nuclear magnetic resonance absorption spectrum of the tetramethyl ester of the benzene adduct in deuterochloroform shows the following proton chemical shifts[7], $\delta = 10^5 (H_r - H_c)/H_r$, measured relative to water at the relative

(7) L. H. Meyer, A. Saika, and H. S. Gutowsky, This Journal, 75, 4567 (1953).

intensities given in parentheses (± 0.5 H atom): + 0.16 (2); doublet at -0.13 (12); -0.195, -0.202, -0.24 (8). The first band is attributable to two ethylenic hydrogen atoms, though the absorption is nearer the value recorded[7] for tiglaldehyde or benzene than for cyclohexene. The band at -0.13 is in the region expected[7] for CH_3O and is of the correct intensity for four methoxyl groups; that this band is split into two bands of essentially equal intensity must mean that two of the methoxyl groups are in one type of environment and two in another (this cannot be ordinary spin-spin splitting because of the isolation of the hydrogen atoms of the methoxyl groups from nearest neighboring hydrogen atoms by at least five intervening bonds). The last group of bands are not well resolved and appear near the region expected[8] for hydrogen on a carbon atom adjacent to a

(8) K. L. Rinehardt, Jr., W. A. Nilsson, and H. A. Whaley, ibid, 80, 503 (1958).

carboxyl or ethylenic group. It is significant that no absorption was found in the region expected for hydrogen on a cyclopropane ring[5,9]. The infrared

(9) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, N. Y., 1959, p. 236.

spectra of the adduct as the anhydride, the acid, or the methyl ester contains no absorption in the 6.73-6.92 region (frequency of CH_2 deformations), while a band appears at 6.80 μ in the hydrogenated acid.

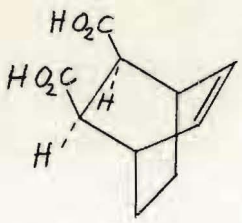
Structures I, II, and III for the adduct from benzene and maleic anhydride are in accord with the principle of minimum structural change. Structure II is eliminated since it does not contain an ethylenic bond as is demanded by the physical and chemical evidence. Structure III is improbable in any of its likely stereochemical forms either because its double bond should be readily attacked by $KMnO_4$ or because it has the two maleic anhydride radicals in equivalent positions. As judged by the behavior of the tetramethyl ester of the benzene adduct with hydrazine, two of the carbomethoxyl groups are considerably more readily attacked by hydrazine than the other two, and these reactive carbomethoxyl groups must be part of the same maleic acid radical since the dihydrazide may be pyrolyzed to a cyclic hydrazide. We are left with structure I as the most probable structure of the adduct in accord with the conclusions of Angus and Bryce-Smith.[2]

Structure I has been more conclusively established by oxidation of a pyridine solution of the tetracarboxylic with lead tetraacetate[10] to give

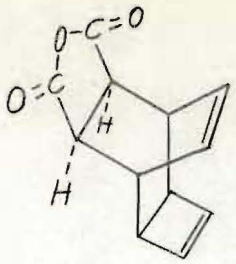
(10) cf. C. A. Grob, M. Ohta, and A. Weiss, Angew. Chem., 70, 343 (1958).

a product of m.p. 168-169°. This product is identical (mixed m.p. and infrared spectral comparisons) with the maleic anhydride adduct (V) of cyclooctatetraene[11].

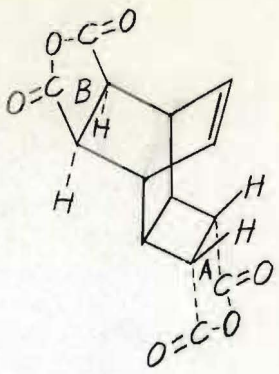
(11) (a) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, Ann., 560, 1 (1948); (b) A. C. Cope and C. G. Overberger, This Journal, 70, 1433 (1948).



(IV)



(V)



(VI)

Of the eight possible stereoisomers of I with cis fusion of the maleic anhydride groups, structure VI seems most probable. The stereochemistry of the maleic anhydride adduct of cyclooctatetraene is evidently that (V) shown since this adduct forms a crystalline rhodium(I) chloride complex, which is believed to involve chelation by the diolefin group[12], and because the adduct

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(12) E. W. Abel, M. A. Bennett and G. Wilkinson, J. Chem. Soc., 3178 (1959).

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forms a monobromolactonic acid.[11a] The position of maleic anhydride group B endo to the double bond is confirmed for the benzene-maleic anhydride adduct by the formation of a bromo-γ-lactone. The location of maleic anhydride group A as shown in VI is implied from the observations: (1) hydrazine readily attacks only two adjacent carbomethoxyl groups of the corresponding tetramethyl ester, (2) lead tetraacetate oxidation removes the two carboxyls of maleic anhydride group A and hence these are implicated as the less hindered carboxyl groups, (3) the alternative location of the carboxyl groups A would place these carboxyl groups very close to the double bond and models indicate that the carboxyl groups A would then be more hindered than the carboxyl groups B. Finally structure VI is confirmed since this structure contains a double bond which is hindered on either side from the approach of external reagents in agreement with the low reactivity of this bond toward permanganate, hydrogen, and halogens.

We are indebted to Dr. Leon Mandell for the nuclear magnetic resonance spectrum.

Erling Grovenstein, Jr.
Durvasula V. Rao
James W. Taylor

School of Chemistry
Georgia Institute of Technology
Atlanta 13, Georgia

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

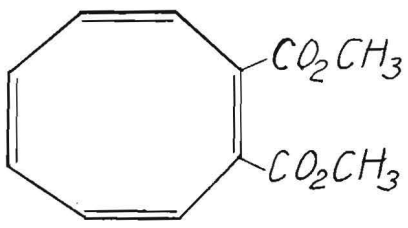
October 14, 1960

Commanding Officer
Office of Ordnance Research, U. S. Army
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 7, Project No. A-421
Photochemically Induced Diels-Alder Reactions
Georgia Tech Research Institute
July 1, 1960 - September 30, 1960
OOR Project No. 2123C, Contract No. DA-01-009-ORD-709

Gentlemen:

Benzene with dimethyl acetylenedicarboxylate upon irradiation with ultraviolet light yields a yellow oil of b.p. 95-150° at 0.03 mm and a non-volatile residue. The yellow oil has recently been formed to crystallize in good part to yellow crystals of m.p. 109.4-110.4° which sublime at 102° at 0.03 mm. These crystals have a satisfactory analysis for $C_{12}H_{12}O_4$ as expected for an adduct from one mole of benzene combined with one mole of dimethyl acetylenedicarboxylate. Also saponification of the yellow oil gives a carboxylic acid of m.p. 206-208°(dec.). This carboxylic acid has elementary analysis and volatility corresponding to the molecular formula $C_{10}H_8O_4$ as expected for an adduct from one mole of benzene combined with one mole of acetylenedicarboxylic acid. In agreement with the analytical data the adduct is tentatively assigned the structure of dimethyl cyclooctatetraene-1,2-dicarboxylate (I):



(I)

REVIEW
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This structural assignment is supported by comparisons of color and ultraviolet and infrared absorption spectra of our acid with that of previously reported cyclooctatetraenemonocarboxylic acid[1]. Upon hydrogenation in acetic acid over a 5% Pt on carbon catalyst, our yellow acid absorbed 2.95 moles of hydrogen per mole of acid in 4 hours and absorbed 0.60 molar equivalents of additional hydrogen in 91 hours; again this behavior is similar to that reported for cyclooctatetraenemonocarboxylic acid[1].

Oxidation of the photochemical adduct anhydride of benzene with maleic anhydride in pyridine solution with lead tetraacetate at 50-66° gives a 56% yield of the maleic anhydride addition product of cyclooctatetraene. This procedure gives a considerable improvement in yield over that which has been previously obtained[2] by oxidation of the tetracarboxylic acid of the benzene-maleic anhydride adduct.

Yours very truly,

Erling Grovenstein, Jr.
Project Director

Approved:

W. C. Whitley, Chief
Chemical Sciences Division

---

1. A. C. Copp, M. Burg, and S. W. Fenton, J. Am. Chem. Soc., 74, 173 (1952).

2. Status Report No. 6 of the present project.

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

January 6, 1961

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 8, Project No. A-421
Photochemically Induced Diels-Alder Reactions
Georgia Tech Research Institute
October 31, 1960 - December 31, 1960
OOR Project No. 2123C, Contract No. DA-01-009-ORD-709

Gentlemen:

A major portion of our time during the period of the present status report was spent in rounding out the experimental details and in writing the enclosed manuscript which is entitled "The Structure and Stereochemistry of the Photochemical Adduct of Benzene with Maleic Anhydride." This manuscript has been accepted for publication in the Journal of the American Chemical Society and is scheduled to appear in April or May, 1961. This paper covers a major part of the experimental work performed under the present contract for the past two years.

In addition, more of the crystalline adduct from dimethyl acetylenedicarboxylate and benzene was prepared and converted to the corresponding dicarboxylic acid. Attempts to decarboxylate the latter are being made, but no definitive results can be reported at the present time.

Yours very truly,

Erling Grovenstein, Jr.
Project Director

Approved:

W. C. Whitley, Chief
Chemical Sciences Division

Enclosure (1)

[Contribution from the School of Chemistry, Georgia Institute of Technology]

The Structure and Stereochemistry of the Photochemical Adduct of Benzene with Maleic Anhydride[1]

(1) This research was supported in part by the Office of Ordnance Research, U. S. Army.

by Erling Grovenstein, Jr., and Durvasula V. Rao, and James W. Taylor

SUMMARY

Benzene combines with two molecules of maleic anhydride under the influence of ultraviolet light to give an adduct which is assigned the structural and stereochemical formula XIV. This structural assignment rests in part upon oxidation of the adduct with lead tetraacetate in pyridine to give a product which is identical with the known maleic anhydride addition product of cyclooctatetraene. The maleic anhydride adduct of cyclooctatetraene is assigned the stereochemical formula XIII. The photochemical adduct XIV of benzene is unusual in that it contains a highly hindered double bond which fails to react with either bromine or potassium permanganate under ordinary conditions of tests for unsaturation.

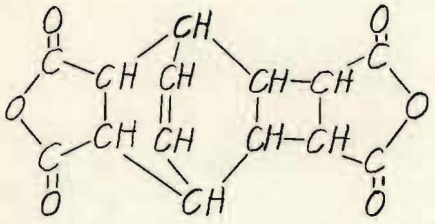
Angus and Bryce-Smith in a recent communication[2] have described the addition

(2) H. J. F. Angus and D. Bryce-Smith, Proc. Chem. Soc., (London), 326 (1959).

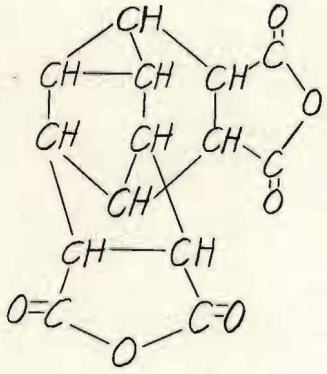
of maleic anhydride to benzene at 60° under the influence of ultraviolet radiation to give a product of m.p. 356° which they provisionally suggest has the structure (I). We have independently discovered this[3] same adduct and wish to report experiments

(3) Our discovery of the 2:1 adduct of maleic anhydride with benzene is contained in the M.S. thesis of J. W. Taylor, Georgia Institute of Technology, June, 1958, and was announced by E. G. at the Seventh Reaction Mechanisms Conference, University of Chicago, September 5, 1958, during the discussion of the paper of Prof. G. Buchi on light-catalyzed organic reactions.

which provide proof for the structure (I) proposed by Angus and Bryce-Smith and which moreover establish the likely stereochemical structure of the adduct.



I



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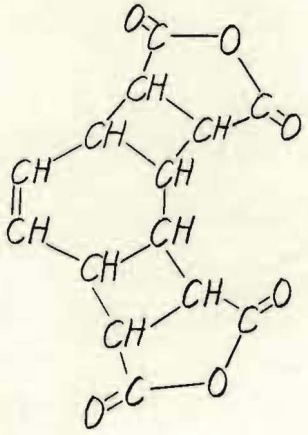


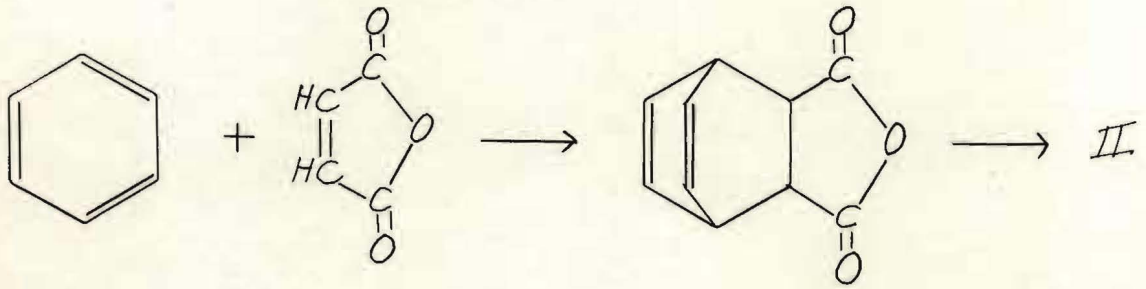
III

V

We have prepared the adduct in 13% yield (based on maleic anhydride) by irradiating for 16 hours with ultraviolet light a nearly saturated solution of maleic anhydride in benzene in a quartz apparatus at room temperature. Larger scale preparations of the adduct in the same apparatus were made in a mixed solvent of acetone and benzene in which maleic anhydride is some ten times more soluble than in benzene alone; acetone seems to have no adverse effect on the yield of product. The adduct is a white crystalline solid of m.p. 355-357° (dec.). It is somewhat soluble in acetone but is essentially insoluble in common organic solvents such as benzene and ether.

The adduct gave correct carbon-hydrogen analyses for $C_{14}H_{10}O_6$ and a saponification equivalent of 68.4 as expected for an adduct from one molecule of benzene combined with two molecules of maleic anhydride. Molecular weight determinations by the melting-point depression technique were unsuccessful in camphor, triphenylethane, β-naphthol, biphenyl or 2,4,6-tribromophenol apparently because the adduct is too insoluble in the melts from these compounds. However the adduct cannot likely have a molecular weight which is two-fold or more that of $C_{14}H_{10}O_6$ because the adduct can be sublimed with only slight decomposition at 240° and 0.02 mm. pressure. Moreover the adduct gives, upon refluxing with 0.08 M methanolic hydrogen chloride, a tetramethyl ester, m.p. 134.5-135.0°, which has correct carbon-hydrogen analyses and molecualr weight (in camphor) for $C_{18}H_{22}O_8$.

The tetracarboxylic acid obtained from saponification of the adduct had satisfactory carbon-hydrogen analyses for $C_{14}H_{14}O_8$ and decomposed at 125-200°, evidently with loss of water, and finally melted at 355-357°(dec.), which is the same as the melting point observed for the adduct anhydride. The acid upon hydrogenation in glacial acetic acid over a 5% platinum on carbon catalyst at room temperature and atmospheric pressure slowly absorbed over a 24-hour period one mole of hydrogen per mole of acid. The anhydride did not decolorize $KMnO_4$ in acetone and showed no reaction with bromine in boiling acetic acid under otherwise the usual conditions for these tests. Similarly, the methyl ester did not decolorize $KMnO_4$ in ethanol nor show any reaction with bromine in methanol in the dark, the latter even after six days. We were led on the basis of these tests for unsaturation to postulate[3] the presence of a cyclopropane ring in our adduct rather than a double bond. A simple structure for the adduct which contains a cyclopropane ring is structure II. This structure could be formed by 1,4-addition of one molecule of maleic anhydride to benzene to give IV and then 1,5-addition of a second molecule of the anhydride to give II:



IV IV

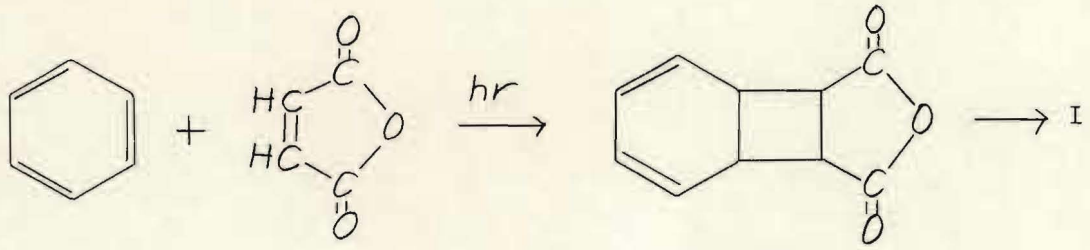
As an analogy for the reaction of IV with maleic anhydride to give II, the thermal addition of maleic anhydride to bicyclo[2,2,1]heptadiene[4] may be cited.

(4) E. F. Ullman, Chem. & Ind. (London), 1173 (1958).

In agreement with a structure such as II, the sodium salt of the tetracarboxylic acid shows no ultraviolet absorption maxima down to 210 mμ but does show "end-absorption" ($\epsilon_{220m\mu} \geq 530$) much like that of the sodium salt of endo-cis-bicyclo[2,2,2]-5-octene-2,3-dicarboxylic acid[5] (V) ($\epsilon_{220m\mu}=390$).

(5) K. Alder and G. Stein, Ann., 514, 15 (1934).

Angus and Bryce-Smith[2] report for the tetracarboxylic acid (?) a weak absorption maximum at 265 mμ ($\epsilon=55$). These workers observed that per-acid titration of the tetramethyl ester indicated the presence of one ethylenic bond per molecule and, on the basis of this information and data rather similar to that given previously, suggested provisionally structure (I) for the adduct. They noted that structure (I) could reasonably be formed by 1,2-addition of one molecule of maleic anhydride to benzene to give VI followed by 1,4-addition of a second molecule of the anhydride to give I:



VI

We would note that VI could conceivably add a second molecule of maleic anhydride by 1,2-addition, rather than by 1,4-addition, to give III rather than I. Furthermore structures I, II, and III can exist in many different stereochemical forms. Finally in view of the known complexity of some photochemical reactions, there is no certainty that the principle of minimum chemical change is not violated in the photochemical reactions leading to the benzene-maleic anhydride adduct. Obviously more detailed studies are necessary to decide between the many possibilities.

The nuclear magnetic resonance spectrum of the tetramethyl ester of the benzene adduct in deuterochloroform shows the following proton chemical shifts[6],

(6) L. H. Meyer, A. Saika, and H. S. Gutowsky, This Journal, 75, 4567 (1953).

$\delta = 10^5$ (Hr-Hc)/Hr, measured relative to water at the relative intensities given in parentheses (expressed as number of hydrogen atoms): +0.16 (1.8); doublet at -0.13 (12.1); -0.195, -0.202, -0.24 (8.1). The first band is attributable to two ethylenic hydrogen atoms, though the absorption is nearer the value recorded[6] for tiglaldehyde or benzene than for cyclohexene. The band at -0.13 is in the region expected[6] for CH_3O and is of the correct intensity for four methoxyl groups; that this band is split into two bands of essentially equal intensity must mean that two of the methoxyl groups are in one type of environment and two are in an appreciably different environment (this cannot be ordinary spin-spin splitting because of the isolation of the hydrogen atoms of the carbomethoxyl groups from nearest neighboring hydrogen atoms by five or more intervening bonds). The last group of bands are not well resolved and appear near the region expected[7]

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(7) K. L. Rinehardt, Jr., W. A. Nilsson, and H. A. Whaley, ibid., 80, 503 (1958).

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for hydrogen on a carbon atom adjacent to a carboxyl or ethylenic group. It is significant that no absorption was found in the region expected for hydrogen on a cyclopropane ring[4,8]. The infrared spectrum of the adduct as the anhydride, the

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(8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, N. Y., 1959, p. 236.

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acid, or the methyl ester contains no absorption in the 6.73-6.92 μ region (frequency of CH_2 deformations[9]), while a band appears at 6.80 μ in the hydrogenated acid.

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(9) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd. ed. Methuen & Co., Ltd., London, 1958, p. 13.

Since the nuclear magnetic resonance absorption spectrum of the tetramethyl ester of the benzene adduct strongly indicates the presence of an olefinic bond and the absence of a cyclopropane ring, the chemical evidence was examined in greater detail. While the sodium salt of the tetracarboxylic acid does not decolorize $KMnO_4$ in 5 minutes at room temperature, some decolorization occurs within a half hour. Similarly the tetracarboxylic acid in dilute hydrochloric acid solution slowly decolorizes bromine-water over a period of several hours. In sharp contrast, the sodium salt of the tetracarboxylic acid in aqueous solution reacts almost instantaneously with bromine to give, after acidification, a bromolactonic

acid which after reaction with excess diazomethane was isolated as a methyl ester VII, m.p. 215-216°. This compound had a satisfactory analysis for carbon, hydrogen, and bromine as calculated for the formula $C_{17}H_{19}BrO_8$ and therefore appears to be a trimethyl ester-bromolactone. This ester has infrared absorption at 5.63 and 5.80 μ near that expected [10] respectively for the carbonyl group of a gamma-lactone and of

(10) Ref. (9) p. 179.

a carbomethoxyl group. Moreover the sodium salt of the tetracarboxylic acid with aqueous I_2-KI solution absorbs in 72 hours at room temperature 9.7% or at 50° 70% of one mole of iodine per mole of acid. In comparative runs under similar conditions the sodium salt of endo-cis-bicyclo[2.2.2]-5-octene-2,3-dicarboxylic acid[5] (V) immediately decolorizes aqueous $KMnO_4$ and absorbs 97% of one molar equivalent of iodine in 23 seconds at room temperature (i.e., iodination occurs about a million times faster with the salt of IV than with the salt of the benzene-maleic anhydride adduct). In conclusion the chemical evidence shows that the benzene-maleic anhydride adduct has one rather highly hindered double bond. Structure II for the adduct can therefore be discarded on the basis of both the chemical data and the nuclear magnetic resonance absorption spectrum.

The tetramethyl ester of the adduct when heated at reflux in methanol containing a large excess of hydrazine gave a 85% yield of a product of m.p. 218-219° (dec.) which gave a fair analysis for a dihydrazide, $C_{16}H_{22}O_6N_4$. The dihydrazide when distilled at 0.01 mm. lost hydrazine and gave a cyclic hydrazide of m.p. 204.7-205.7° which gave a good analysis for $C_{16}H_{18}O_6N_2$. The cyclic hydrozide when heated at reflux in methanol containing a large excess of hydrazine deposited crystals (87% yield) of the starting dihydrazide. As judged by the behavior of the tetramethyl ester with hydrazine, two of the carbomethoxyl groups are considerably more readily attacked by hydrazine than the other two, and these reactive carbomethoxyl groups must be part of the same maleic acid radical since the dihydrazide may be pyrolyzed to a cyclic hydrazide. The chemical evidence, therefore, supports the nuclear magnetic resonance absorption data in indicating that two of the carbomethoxyl groups of the tetramethyl ester are in an appreciably different environment than the other two carbomethoxyl groups. These data render structure III improbable in any of its likely stereochemical forms either because its double bond should be readily attacked by $KMnO_4$ or because it has two maleic anhydride radicals in equivalent positions. Of the structures for the benzene-maleic anhydride adduct which are in accord with the principle of minimum structural change, we are left with structure I as the most probable structure.

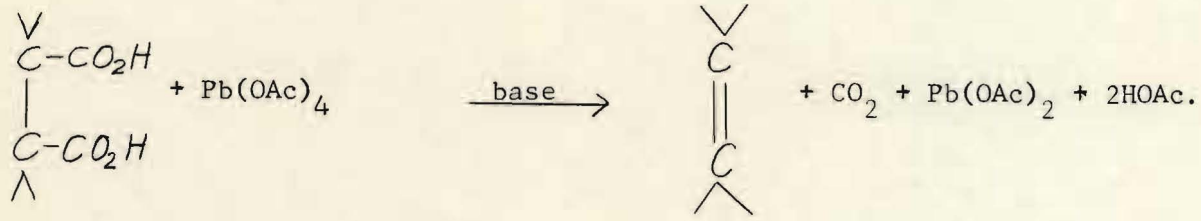
Much more conclusive evidence for the structure of the adduct has been provided by oxidation[11] of a pyridine solution of the tetracarboxylic acid or better the

(11) We are indebted to Mr. Gary G. Hammer and Dr. Leon H. Zalkow for pointing out to us the method of Grab and co-workers and to Dr. Jack Hine for suggesting the use of pyridine as a solvent for this reaction.

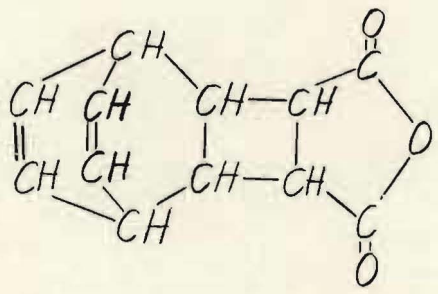
the adduct anhydride itself with lead tetraacetate. Grob[12] and co-workers have reported

(12) C. A. Grob, M. Ohta, and A. Weiss, Angew. Chem., 70, 343 (1958).

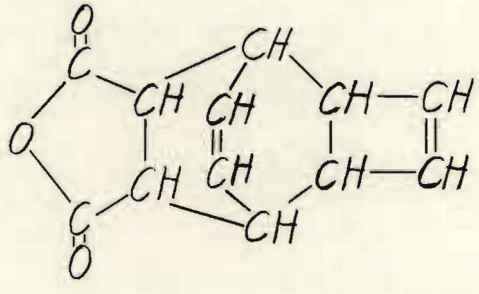
that oxidation of several cis-1,2-dicarboxylic acids in presence of one to two molar equivalents of a base such as pyridine in benzene or acetonitrile as solvent gave 50-70% yield of olefin in accord with the process:



From oxidation of the benzene-maleic anhydride adduct with lead tetraacetate in pyridine at 50 to 62°, 56% yield was obtained of a product of m.p. 167-168.7° which had satisfactory analysis for $C_{12}H_{10}O_3$. The same product, but in lower yield, was obtained by oxidation of the tetracarboxylic acid. During the lead tetraacetate oxidation, therefore, only one of the two maleic anhydride radicals of the adduct was oxidized. On the basis of structure I for the adduct, the lead tetraacetate oxidation could give either VIII or IX for the product of composition $C_{12}H_{10}O_3$. Structure IX can exist in four stereochemical forms (involving cis-fusion of the four-and five-



VIII



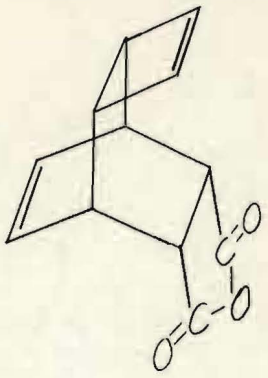
IX

membered rings to the[2,2,2] bicyclooctene system), one of these forms corresponds to the known[13] maleic anhydride adduct of cyclooctatetraene. It is remarkable,

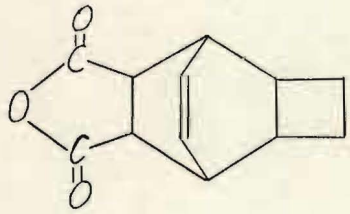
(13) (a) W. Reppe, O. Schlichting, K. Klager, and T. Toeppel, Ann., 560, 1 (1948); (b) A. C. Cope and C. G. Overberger, This Journal, 70, 1433 (1948).

therefore, that the product $C_{12}H_{10}O_3$ from lead tetraacetate oxidation of the benzene-maleic anhydride adduct was found to be identical (mixed m.p. and infrared spectral comparisons) with the maleic anhydride adduct of cyclooctatetraene. This evidence conclusively establishes the structure of the benzene-maleic anhydride adduct as I in agreement with the brilliant provisional suggestions of Angus and Bryce-Smith[2]. There remains unanswered the question of the stereochemical structure of the photochemical adduct.

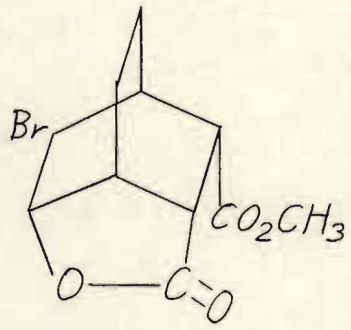
Structure I can exist in eight possible stereoisomeric forms with cis-fusion of the maleic anhydride groups. A key to the stereochemical form of the benzene-maleic anhydride adduct is found in the stereochemistry of the cyclooctatetraene-maleic anhydride adduct IX. Reppe[13a] and co-workers reported that this adduct gives a bromolactonic acid; therefore, the carboxyl groups of the adduct must be located in close proximity to one of the double bonds of the adduct. These workers have proposed that the cyclooctatetraene-maleic anhydride adduct has the stereochemical formula X and, therefore, that bromolactone formation involves attack of bromine



X



XI



XII

on the double bond in the six-membered ring to give a γ-lactone. Cope[14] and co-workers

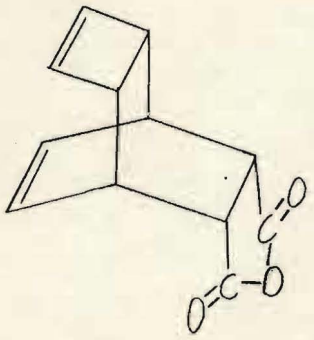
(14) A. C. Cope, A. C. Haven, Jr., F. L. Ramp, and E. R. Trumbull, ibid., 74, 4867 (1952).

have proven that hydrogenation of the cyclooctatetraene-maleic anhydride adduct under mild conditions adds a mole of hydrogen to the double bond of the four-membered ring to give XI rather than to the double bond of the six-membered ring as previously supposed[13a]. Hence Cope et al. have pointed out that bromolactone formation may involve addition of bromine to the double bond of the four-membered ring; if this is the case, the bromolactone of IX is a delta-lactone. To distinguish between these possibilities we have examined the infrared absorption spectrum of the mono-methyl ester[13a] of the bromolactone of IX. This compound has carbonyl absorption at 5.69 and 5.76 μ. The first value agrees somewhat more closely with the absorption expected[10] for a γ-lactone (5.62-5.68 μ) than that for a δ-lactone (5.71-5.76 μ), while the second value corresponds to the value expected for the carbonyl groups of an ester. We find that the bromolactonic ester XII of endo-cis-bicyclo[2.2.2]-5-octene-2,3-dicarboxylic acid[5] (V) has carbonyl absorption at 5.69 amd 5.79 μ; hence γ-lactones in polycyclic systems may give carbonyl absorption at 5.69 μ as found for the cyclooctatetraene adduct.

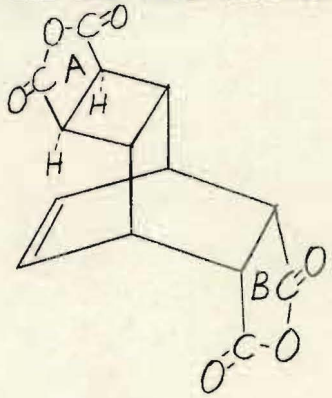
To provide more conclusive proof of the stereochemistry of IX, the reaction of the dihydro derivative XI with bromine has been investigated. Of the four possible stereoisomers of IX with cis orientation of the carbonyl groups, it may be seen that the carbonyl groups of the corresponding acid may be oriented near one or the other or none of the double bonds but cannot be oriented for a particular isomer such that bromolactone formation can take place with either double bond. Hence one method for determining which double bond is oriented near to the carbonyl groups is to remove one double bond by hydrogenation and see if the corresponding dihydro-derivative can form a bromolactone. Cope and co-workers evidently had this strategy in mind when they reported[14] that dihydro-derivative XI "does not react readily with bromine", but did not specify the conditions tried. Because of our previous experience in bromination of the benzene-maleic anhydride adduct (see earlier discussion), we were led to reinvestigate the bromination of XI. While XI did not decolorize a solution of bromine in CCl_4 or acetic acid in 3 hours the potassium salt of XI in water reacted almost instantaneously with one molar equivalent of bromine to give a good yield of a crystalline product of m.p. 243-244°(dec.), which had the expected composition for a bromolactonic acid, $C_{12}H_{13}O_4Br$. The corresponding crystalline mono-methyl ester, $C_{13}H_{15}O_4Br$, had carbonyl absorption at 5.65 and 5.77 μ as expected for the methyl ester of a γ-lactone. Hence the carbonyl groups of IX are oriented near to the double bond in the six-membered ring rather than near the double bond of the four-membered ring. Thus structure X of Reppe[13a] et al. is correct in so

far as this particular structural detail is concerned.

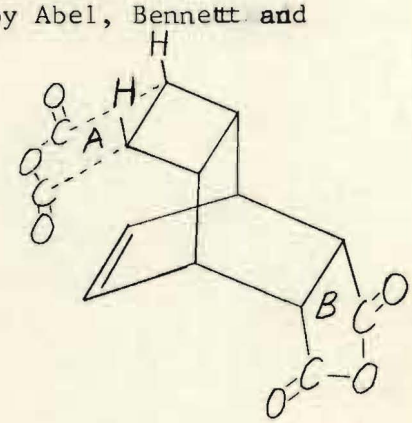
There was never, however, any compelling evidence for the steric orientation of the four-membered ring of X relative to the cyclohexene ring. Structure XIII would appear to be equally probable and has been written by Abel, Bennett and



XIII



XIV



XV

Wilkinson[15]. These workers have found that the cyclooctatetraene-maleic anhydride

(15) E. W. Abel, M. A. Bennett and G. Wilkinson, J. Chem. Soc., 3178 (1959).

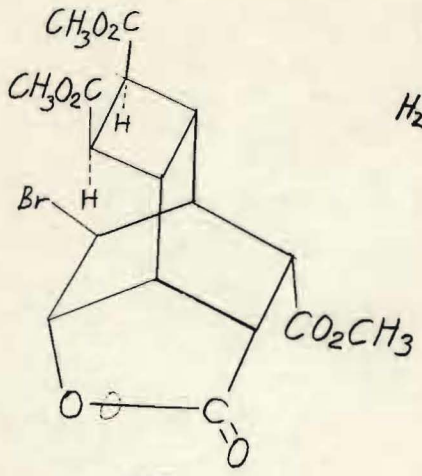
adduct forms a crystalline rhodium(I) chloride complex which is believed to involve chelation by the diolefin group to one rhodium atom. The two double bonds in the cyclooctatetraene-maleic anhydride adduct are, therefore, almost certainly oriented as in XIII especially since bicyclo [2.2.1]-heptadiene (norbornadiene) forms a similar rhodium(I) chloride complex[15].

If no changes in steric orientation of groups occur during the oxidation of the benzene-maleic anhydride adduct (I) by lead tetraacetate to give XIII, then only structures XIV and XV need be considered for the photochemical adduct. No changes in stereochemistry are expected to occur during the lead tetraacetate oxidation because of the mild conditions of the reaction and the speed of the oxidative decarboxylation. These expectations appear to be confirmed since the tetracarboxylic acid of I gave XIII as only insoluble acidic product while at least some of the trans-acid[13a] would have been expected if any isomerization had occured at the centers bearing the carboxyl groups. Furthermore the photochemical adduct I gave a bromo-γ-lactone and hence one acid anhydride group in I must be oriented as in XIII. Of the two structures XIV and XV, structure XIV appears much more probable than XV. The location of anhydride group A as in XIV rather than as XV is implied

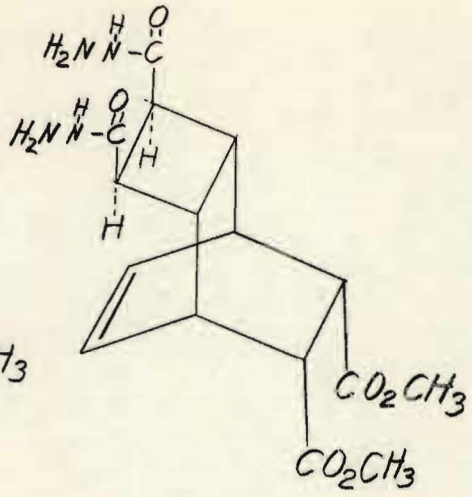
from the observations: (1) hydrazine readily attacks only two adjacent carbomethoxyl groups of the corresponding tetramethyl ester, (2) lead tetraacetate oxidation removes the two carbonyl groups of anhydride group A and hence these are implicated as the less hindered carbonyl groups, (3) the alternative location of the carbonyl groups A as in XV would place these goups very close to the double bonds and models indicate that the carbonyl groups A would then be more hindered than the carbonyl groups B, (4) bromolactone formation gives a γ-lactone as expected from XIV while a δ-lactone might be expected from XV.

In conclusion structure XIV is assigned as the probable stereochemical structure of the photochemical adduct of benzene with maleic anhydride. This structure contains a double bond which is hindered on either side from the approach of external reagents. Structure XIV, therefore, accounts for the remarkable unreactivity of the double bond toward permanganate and halogens. The structures of some of the other compounds prepared in the present work are summarized in Chart 1 and certain of these structural assignments are discussed in the Experimental Details.

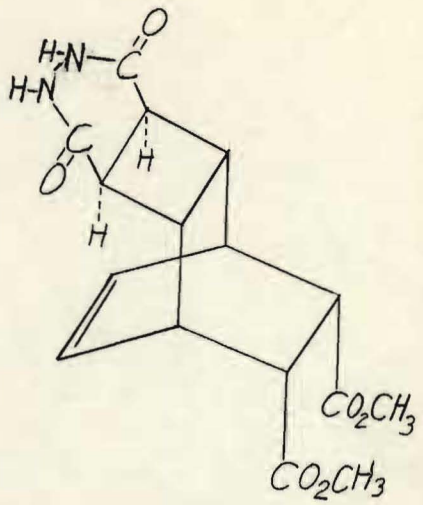
CHART 1



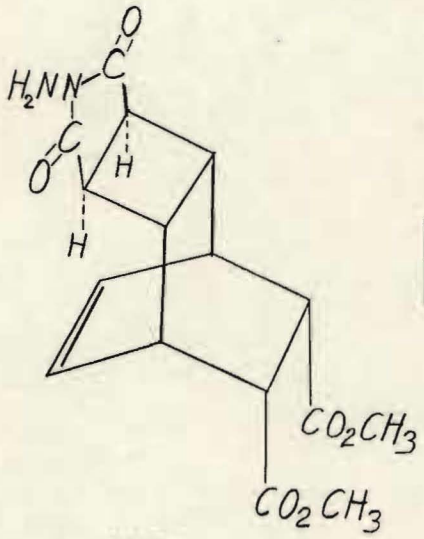
VII



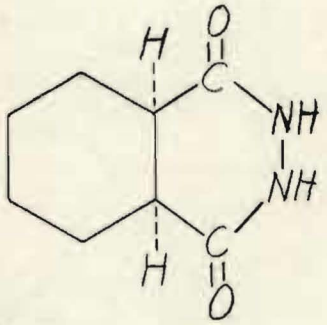
XVI



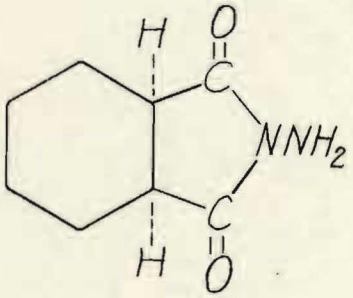
XVIIa



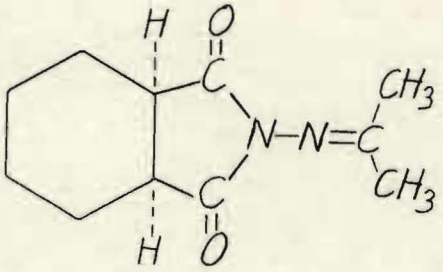
XVIIb



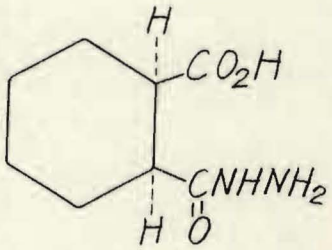
XVIIIa



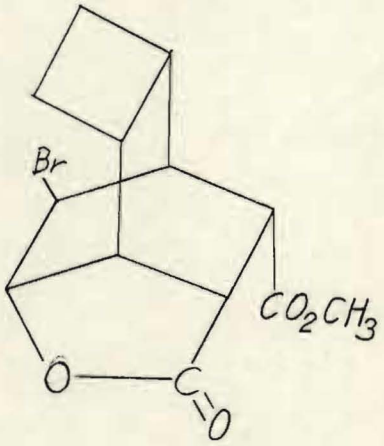
XVIIIb



XIX



XX



XXI

Experimental Details[16]

(16) All melting points are corrected. Analyses are by Clark and Galbraith Microchemical Laboratories.

Benzene-Maleic Anhydride Adduct (XIV).—Maleic anhydride (10.0 g., 0.102 moles) was dissolved in 300 ml. of thiophene-free benzene. The solution was placed in a water-cooled quartz cell which encircled a 1000-watt Hanovia mercury-arc lamp[17].

(17) For a more detailed description of the apparatus see E. Grovenstein,Jr., and S. P. Theophilou, This Journal, 77, 3795 (1955).

The solution was irradiated for 16 hours. During this time white crystals precipitated on the walls of the cell. The precipitate of XIV was separated by filtration and washed with three 25 ml. portions of boiling benzene. The yield of XIV was 1.90 g. or 13.6% of product of m.p. 355-357° (dec).

For larger scale preparations 118 g. (1.20 moles) of freshly distilled maleic anhydride was dissolved in 100 ml. of acetone (which had been purified by distillation from $KMnO_4$) and 125 ml.(1.4 moles) of thiophene-free benzene was added. The solution after irradiation in the apparatus described above for 25 hours deposited 10.5 g. of adduct which was separated by filtration. Another 6.5 g. of adduct was recovered by evaporation of the solvent, boiling the residue with about 200 ml. of acetone to dissolve unreacted maleic anhydride, and separation of the adduct by filtration. The yield of product (17.0 g.) was 10.3 %. In similar runs with 120 g. of maleic anhydride and an irradiation time of 48 hours 16.0 to 18.0 g. of adduct deposited in the cell but only some 1.5 g. of additional adduct was recoverable from the reaction solution.

The adduct when thoroughly washed with hot benzene or acetone did not decolorize dilute solutions of $KMnO_4$ in acetone; however, maleic anhydride readily decolorizes such $KMnO_4$ solutions and thus the permanganate test is a convenient test for the purity of the adduct from the present preparations. The adduct sublimed slowly at 0.015 mm. and a bath temperature of 240-250° to give a product of m.p. 355-357° (dec.), while at higher temperatures a brown product was obtained.

Anal. Found: C, 61.24, 61.37; H, 3.64, 3.74; saponification equiv., 68.4. Calcd. for $C_{14}H_{10}O_6$: C, 61.32; H, 3.68; saponification equiv. for tetrabasic acid anhydride, 68.55.

Tetramethyl Ester of XIV.— The benzene-maleic anhydride adduct (1.80 g.) was esterfied by boiling under reflux with anhydrous methanol (100 ml.), which was 0.078 M in anhydrous hydrogen chloride, for six hours. The solution was concentrated to 20 ml. and, on cooling, 1.58 g. of white crystals, m.p. 130-132°, precipitated. Recrystallization three times from anhydrous methanol gave methyl ester of m.p. 134.5-135.0°. This product sublimed readily at a bath temperature of 200° and a pressure of 0.015 mm.

Anal. Found: C, 58.82, 58.91; H, 5.88, 5.89; mol. wt., 366 (determined in camphor, with triphenylmethane used to determine the melting-point depression constant). Calcd. for $C_{18}H_{22}O_8$: C, 59.01; H, 6.05; mol. wt., 366.4

The tetracarboxylic acid of XIV (see below) upon esterification with methanolic hydrogen chloride by a rather similar procedure gave a methyl ester of m.p. 133.0-133.4° which showed no m.p. depression with the methyl ester prepared from the anhydride and, moreover, had an identical infrared absorption spectrum.

Tetracarboxylic Acid of XIV.— The benzene-maleic anhydride adduct (25.5 g., 0.0929 mole) was heated at reflux with 254 ml. of 1.46 M aqueous KOH (0.372 mole) with occasional shaking for 5 hours. The solution was cooled and filtered to remove a small amount of suspended solid. The solution upon acidification with hydrochloric acid yielded a fine crystalline precipitate. The precipitate was separated and recrystallized from water to give 20.0 g. of crystals. After two additional crystallizations from water, the product showed decomposition at 125-200° ($-H_2O$) and finally melted at 350-353° (dec.). The analytical sample was recrystallized two more times from water and had m.p. 356-357° (dec.) with previous loss of water near 120°.

Anal. Found: C, 54.46, 54.69; H, 4.16, 4.21. Calcd. for $C_{14}H_{14}O_8$: C, 54.20; H, 4.55.

The tetracarboxylic acid (0.553 g.) in 80 ml. of glacial acetic acid was hydrogenated at room temperature over 0.49 g. of a 5% Pt on charcoal catalyst. After 24 hours the sample had absorbed 36.9 ml. (S.T.P.) of hydrogen or 0.925 mole of hydrogen per mole of acid taken. No more hydrogen was absorbed in an additional 72 hours. An analysis of the particular sample of tetracarboxylic acid taken

gave: C, 49.99; H, 4.38; ash, 7.4. After correction for ash, the analytical data became C, 53.98; H, 4.73; 1.00 mole of hydrogen absorbed per mole of acid. From the hydrogenation mixture an acid of m.p. 295-297° (dec.) was isolated; this dihydro acid was considerably more soluble in acetic acid than the starting acid and was converted into an acid anhydride upon heating with acetic anhydride.

Bromolactone Trimethyl Ester (VII) of XIV. — The tetracarboxylic acid of XIV, 1.52 g. or 4.9 mmoles, was dissolved in about 20 ml. of aqueous sodium hydroxide and the excess of base was neutralized with hydrochloric acid to pH 9. Bromine was added slowly with shaking until a pale yellow color of bromine remained (0.24 ± .02 ml. of bromine added or some 4.7 mmoles). The bromine color was almost instantaneously discharged at first but near the end of the addition the color remained a short while. The solution was acidified with 10 ml. of concentrated hydrochloric acid and evaporated to dryness in the steam bath. The residue was ground up and extracted several times with, in all, 55 ml. of tetrahydrofuran. A solution of diazomethane in ether was added to the tetrahydrofuran solution until a yellow color persisted. Evaporation of the solvents gave white crystals which were partially dissolved by 125 ml. of hot methanol. Filtration of the cooled solution gave 1.07 g. of white crystals of m.p. 211-215°. After two crystallizations from benzene the product had m.p. 215.0-216.3°.

Anal. Found: C, 47.11, 47.19; H, 4.35, 4.41; Br, 18.52, 18.59. Calcd. for $C_{17}H_{19}BrO_8$: C, 47.34; H, 4.44; Br, 18.53.

Iodolactone Formation by XIV and V. — The sodium salts of the anhydrides of XIV and V were prepared by heating the anhydride with some 30% excess sodium hydride solution and back-titration with hydrochloric acid almost to the disappearance of the color of phenolphthalein. For iodolactone formation one volume of the sodium salt of XIV or V was mixed with an equal volume of iodine-potassium iodide solution to give an initial solution which was 0.018 M in the salt of XIV or V, 0.025 M in iodine, and 0.137 M in sodium iodide. For measurement of the consumption of iodine, slow iodinations were acidified with acetic acid and titrated with thiosulfate to a starch end-point, while fast reactions were made strongly acidic with hydrochloric acid before titration of unreacted iodine.

Reaction of Tetramethyl Ester of XIV with Hydrazine. — The tetramethyl ester of XIV (2.00 g.) was heated at reflux with 5.0 ml. of 98% hydrazine in 25 ml. of methanol for two hours. A white precipitate separated during the reaction and after separation by filtration from the cold reaction mixture amounted to 1.70 g. (85% yield) of compound of m.p. 218 - 219° (dec.). This compound XVI appears

to be a dihydrazide dimethyl ester of XIV and was found to be identical (mixed m.p. and infrared spectral comparisons) with the compound of similar m.p. prepared below by reaction of hydrazine with the cylic hydrazide XVII. Compound XVI was soluble in water and acetic acid but was essentially insoluble in solvents such as benzene and methyl alcohol. Since attempts to recrystallize XVI from common solvents were unsuccessful, a 1.3 g. sample of XVI was subjected to vacuum sublimation at 0.01 mm. and a bath temperature of 270°. Sublimation was complete in 0.5 hrs. The sublimate was taken up in 25 ml. of hot methanol. The solution was filtered to remove a small amount of insoluble material and on cooling deposited white crystals. After two recrystallizations from methanol the product amounted to 1.0 g. of material of m.p. 202.7-203.7°. The analytical sample was recrystallized two more times from methanol and sublimed four times (at 240° and 0.01 mm.) to give cyclic hydrazide XVII (structure XVIIa or XVIIb) of m.p. 204.7-205.7°.

Anal. Found: C, 57.65; H, 5.55; N, 8.32. Calcd. for $C_{16}H_{18}O_6N_2$: C, 57.48; H, 5.43; N, 8.38.

Compound XVII (0.50 g.) was dissolved in 25 ml. of methanol. To the solution was added 2.0 ml. of 98% hydrazine and the mixture was heated at reflux for 1.5 hr. during which time a white precipitate appeared. Filtration of the cooled solution gave 0.48 g. (87% yield) of white crystals of XVI of m.p. 218-219° (dec.)[18].

Anal. Found: C, 51.80; H, 6.01; N, 15.36. Calcd. for $C_{16}H_{22}O_6N_4$: C, 52.45; H, 6.05; N, 15.29.

The tetramethyl ester of XIV (2.0 g.) was heated at reflux with 5.0 ml. of 98% hydrazine for 15 min. Methanol (20 ml.) was added and the reaction mixture was heated at reflux for 3 hrs. The dull white solid which separated amounted to 1.6 g. The product was boiled with 10 ml. of absolute methanol and on separation by filtration was a pure white solid of m.p. 211-213° (dec.). The material did not sublime or distill at temperatures up to 300° at 0.015 mm. and and may therefore be a polymer. The product had almost as much nitrogen as expected for the tetrahydrazide of XIV.

Anal. Found: N, 28.30. Calcd. for $C_{15}H_{22}O_5N_6$: N, 22.94; calcd. for $C_{14}H_{22}O_4N_8$: 30.59.

The reaction of the dimethyl ester of cis-hexahydrophthalic acid with hydrazine was studied as a model to aid in understanding the reactions of the tetramethyl ester of XIV with hydrazine.

Cyclic Hydrazide XVIII of cis-Cyclohexane-1,2-dicarboxylic Acid.-Dimethyl cis-cyclohexane-1,2-dicarboxylate (5.0 g.) was heated with 5.0 ml. of 98% hydrazine at

reflux for 15 min. Just enough methanol was added to give a homogeneous solution and the mixture was heated at reflux for one hour. Concentration of the solution gave a crystalline product which, after one recrystallization from 85% methanol, amounted to 4.8 g. of dihydrazide of m.p. 229-230° (dec.) (recorded: trans[18a], 229-31°; cis[18a], 123-4.5° and then 228.5-229.5°; unspecified isomer [18b], 245°). The

(18)(a) V. G. Iashunskii, J. Gen. Chem. U.S.S.R. (Eng. Transl.), 28, 1420 (1958); (b) H. Wieland, O. Schlichting, W. v. Langsdorff, Z. physiol. Chem., Hoppe-Seyler's, 161, 78 (1926). The m.p. of our dihydrazide of cyclohexane-1,2-dicarboxylic acid was variable with the rate of heating. At a fast rate of heating the m.p. was some 15° higher than the value reported above. Similar observations were made with respect to the m.p. of dihydrazide XVI.

dihydrazide (45 g.)from a similar large-scale preparation was pyrolyzed at a bath temperature of 280-290° and a pressure of 20 mm. to give distillate of b.p. 220-230° at 20 mm. The distillate (30 g.) solidified on cooling and had m.p. 55-60°. A second distillation gave a colorless product of b.p. 152-160° at 0.5 mm. and of m.p. 60-63°. Redistillation through a short fractionating column gave cyclic hydrazide XVIII of m.p. 60.4-62.9°.

Anal. Found: C, 57.42; H, 7.02; N, 16.42, Calcd. for $C_8H_{12}O_2N_2$: C, 57.13; H, 7.19; N, 16.66.

The cyclic hydrazide XVIII (3.0 g.) was dissolved in 30 ml. of concentrated hydrochloric acid and the mixture heated at reflux for 15 minutes. The solid which precipitated was separated by filtration of the cool solution and was washed with water. The product (2.6 g.) had m.p. 187.3-188.7° as expected for cis-cyclohexane-dicarboxylic acid (recorded[18a], m.p. 189.5-190.5°). Similar treatment of our starting dihydrazide of cyclohexane-1,2-dicarboxylic acid (3.0 g.) with 30 ml. of concentrated hydrochloric at reflux for 30 minutes gave 1.3 g. of product of m.p. 182-204°. This product upon sodium fusion gave a negative test for nitrogen and halogen and thus appears to be a mixture of cis- and trans-cyclohexane-1,2-dicarboxylic acids.

For an attempted purification by recrystallization, XVIII was dissolved in a minimum amount of acetone and two volumes of n-hexane was added. The mixture was heated on a steam bath and the supernatant hexane layer was separated. Two similar hexane extractions were made and from the combined hexane extracts crystals in the form of needles were obtained on cooling. These after another similar crystallization from acetone-n-hexane had m.p. 124.0-125.5° (with previous sintering at 120°).

Anal. Found: C, 63.89; H, 7.98; N, 13.12. Calcd. for $C_{11}H_{16}O_2N_2$: C, 63.44; H, 7.74; N, 13.45.

This product has an analysis corresponding to that of an isopropylidene derivative of XVIII. The only likely structure for the isopropylidene derivative appears to be XIX. The ready formation of XIX from XVIII suggests that XVIII has structure XVIIIb rather than the isomeric structure XVIIIa. However, since Drew and Hatt[19] have shown that the more stable phthalhydrazide gives the same

(19) H. D. K. Drew and H. H. Hatt, J. Chem. Soc., 16 (1937).

benzylidine derivative as the less stable N-aminophthalimide though under more vigorous conditions, the reaction of XVIII with acetone cannot be regarded as affording proof of structure XVIIIb.

The potentiometric titration of succinhydrazide as a monobasic acid has been cited[20] as evidence in favor of the hydrazide structure as opposed to the N-amino-

(20) H. Feuer, G. B. Bachman, and E. H. White, This Journal, 73, 4716 (1951).

succinimide structure. We find that XVIII, when dissolved in excess sodium hydroxide and back-titrated potentiometrically with hydrochloric acid, gives a neutralization equivalent of 172 (theory for monobasic acid $C_8H_{12}O_2N_2$, 168). The direct titration of XVIII with sodium hydroxide is difficult since XVIII combines rather slowly with the base and our titrimetric data indicate that XVIII undergoes hydrolysis to give the salt of XX under the conditions of the titration. Since either XVIIIa or XVIIIb might be expected to undergo ready hydrolysis to XX, the titration is also unable to distinguish between the two likely structures for XVIII.

Oxidation of XIV with Lead Tetraacetate.- The anhydride XIV (5.0 g., 0.0182 mole) was dissolved in 200 ml. of hot pyridine (which had been dried over KOH pellets and freshly distilled). Lead tetraacetate (9.0 g., 0.020 mole) was added and the pyridine solution was maintained at 70-80° for one hour. During the first five minutes of reaction there was a vigorous evolution of carbon dioxide. The solvent was removed in vacuo with aid of a steam bath. The dark brown residue was acidified with hydrochloric acid and extracted with ether three times. The etheral extracts were combined, washed with water twice, and dried over anhydrous $MgSO_4$. After removal of the ether, 1.5 g. of crystalline product was obtained. This was sublimed at 0.025 mm. at a bath temperature of 170° to give 1.45 g. (39.5% yield) of crystalline sublimate. After two recrystallizations from chlorobenzene the product XIII had m.p. 166.9-168.7.

Anal. Found: C, 70.89, 70.92; H, 4.80, 4.95. Calcd. for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98.

A sample of the maleic anhydride addition product of cyclooctatetraene was prepared[13] by heating maleic anhydride with cyclooctatetraene under a nitrogen atmosphere at a bath temperature of 180° for 30 min. The product after sublimation in vacuo and recrystallization from chlorobenzene had m.p. 167.3-168.7° and gave no depression of m.p. when mixed with the product from the lead tetraacetate oxidation. Likewise the two products had identical infrared spectra.

A higher yield was obtained from reaction of 2.40 g. (0.00875 mole) of the anhydride XIV with 5.8 g. (0.013 mole) of lead tetraacetate in 85 ml. of pyridine maintained at 50-60° for one hour. The reaction mixture after standing over night was worked up as previously. After one sublimation in vacuo , the product amounted to 1.00 g. (56% yield) of material of m.p. 166.6-168.3°. A similar oxidation with lead tetraacetate in which 2 moles of lead tetraacetate were used per mole of anhydride gave only 34% yield of XIII.

Oxidation of the tetracarboxylic acid of XIV with lead tetraacetate was hindered, at least in part, by the low solubility of the acid in pyridine. Tetracarboxylic acid (5.0 g., 0.0161 mole) did not dissolve very completely in 150 ml. of boiling pyridine. To the mixture at 95-100° was added 10.0 g. (0.023 mole) of lead tetraacetate and the reaction mixture was kept at this temperature for one hour. The reaction was worked up as with the anhydride. From the ether extracts 0.50 g. of crude product was obtained. After one recrystallization from methanol the product amounted to 0.35 g. of material of m.p. 160-161.5°. Another recrystallization from methanol gave a product XIII of m.p. 167.1-167.9° which was identical with the maleic anhydride adduct of cyclooctatetraene (mixed m.p. and infrared-spectral comparisons).

Bromolactone of XI. -The dihydro derivative[14] of the maleic anhydride adduct of cyclooctatetraene (XI), 2.00 g. (0.0098 mole) of m.p. 142.5-143.5°, was dissolved in a warm solution of 3 g. of KOH in 50 ml. of water and the solution was filtered to remove a trace of suspended material. The solution was neutralized to a phenolphthalein end-point with hydrochloric acid and bromine was added dropwise with shaking. The color of bromine disappeared rapidly during addition of 0.45 ml. (8.8 mmoles) but a permanent yellow color remained after addition of 0.05 ml. (1.0 mmole) more bromine. Acidification gave a precipitate which after separation by filtration and recrystallization from 95% ethanol amounted to 2.50 g. (85% yield) of bromolactonic acid of m.p. 243.3-243.8° (dec.).

Anal. Found: C, 47.73, 47.81; H, 4.52, 4.40; Br, 26.61. Calcd. for $C_{12}H_{13}O_4Br$: C, 47.86; H, 4.35; Br, 26.54.

The bromolactonic acid was dissolved in tetrahydrofuran and a solution of diazomethane in ethyl ether was added until a pale yellow color persisted. The solvents were removed by evaporation and the resulting crystalline residue was recrystallized twice from methanol to give methyl ester XXI of m.p. 166.9 -167.9°.

Anal. Found: C, 49.45, 49.63; H, 4.80, 4.96; Br, 25.25. Calcd. for $C_{13}H_{15}O_4Br$: C, 49.54, H, 4.80; Br, 25.35.

Spectra.- Infrared spectra were run with samples in potassium bromide disks on a Perkin-Elmer model 21 infrared spectrometer with rock-salt prisms. Ultraviolet spectra were determined on a Beckman model DK-1 quartz spectrophotometer. The nuclear magnetic resonance absorption spectrum was determined on a Varian frequency R-F unit model V4310C with frequency of 40 megacycles and a field of 10,000 gauss. The tetramethyl ester of XIV (0.1 g.) was dissolved in 0.3 ml. of $DCCl_3$ and the chemical shifts were determined relative to $HCCl_3$ which was contained within an inner concentric tube. For calculations of chemical shifts relative to water chloroform was taken to have a chemical shift of 96 cycles/sec. at 40 Mc.

Acknowledgement.-We are indebted to Dr. Leon Mandell for the nuclear magentic resonance spectrum.

FINAL REPORT

PROJECT NO. A-421

PHOTOCHEMICALLY INDUCED DIELS-ALDER REACTIONS

By

ERLING GROVENSTEIN, JR, and DURVASULA V. RAO

JANUARY 2, 1959 through JANUARY 1, 1961

CONTRACT NO. DA-01-009-ORD-709
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DJV

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

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SUMMARY

The aim of the present work was to investigate the feasibility of using ultraviolet light to bring about Diels-Alder reactions between dienes and dienophiles which either do not react or react in poor yield or in other manner by the ordinary thermally induced process. For convenience the present work is described in three parts.

Part I deals with "The Structure and Stereochemistry of the Photochemical Adduct of Benzene with Maleic Anhydride." This adduct consists of two molecules of maleic anhydride combined with one of benzene and has been proven to have the structure tricyclo ($4.2.2.0^{2,5}$) dec-9-ene-3,4,7,8-tetracarboxylic acid dianhydride (for structural and steoreochemical formula see formula XIV p. 10 of Part I). Thus this product is formed by 1,2- as well as by 1,4-addition (Diels-Alder type addition) of maleic anhydride to benzene. Part I is a reproduction of a paper which has been accepted for publication in the Journal of the American Chemical Society.

Part II concerns "A Preliminary Search for Reaction of Maleic Anhydride with Thiophene, Chlorobenzene, Toluene, p-xylene, and Naphthalene upon Irradiation with Ultraviolet Light." Maleic anhydride was found to undergo reaction with thiophene, chlorobenzene, toluene, and p-xylene when irradiated with ultraviolet light at room temperature. No product, however, was isolable from the corresponding attempted reaction of maleic anhydride with naphthalene. While mixtures of products appear to be obtained in all cases, the product from toluene was found to consist of some 67% of benzylsuccinic anhydride while that from p-xylene was at least 50% by weight of p-methylbenzylsuccinic anhydride.

Part III describes the "Photochemical Reaction of Dimethyl Acetylenedicarboxylate with Benzene." Dimethyl acetylenedicarboxylate reacts with benzene at room temperature under irradiation by ultraviolet light to give, among other products, a substance which is provisionally assigned the structure of dimethyl cyclooctatetraene-1,2-dicarboxylate. Thus dimethyl acetylenedicarboxylate undergoes a novel 1,2- or (dependent upon the point of view) 1,6- addition to benzene.

TABLE OF CONTENTS

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Part I

[Contribution from the School of Chemistry, Georgia Institute of Technology]

The Structure and Stereochemistry of the Photochemical Adduct of Benzene with Maleic Anhydride[1]

(1) This research was supported in part by the Office of Ordnance Research, U. S. Army.

by Erling Grovenstein, Jr., and Durvasula V. Rao, and James W. Taylor

SUMMARY

Benzene combines with two molecules of maleic anhydride under the influence of ultraviolet light to give an adduct which is assigned the structural and stereochemical formula XIV. This structural assignment rests in part upon oxidation of the adduct with lead tetraacetate in pyridine to give a product which is identical with the known maleic annydride addition product of cyclooctatetraene. The maleic anhydride adduct of cyclooctatetraene is assigned the stereochemical formula XIII. The photochemical adduct XIV of benzene is unusual in that it contains a highly hindered double bond which fails to react with either bromine or potassium permanganate under ordinary conditions of tests for unsaturation.

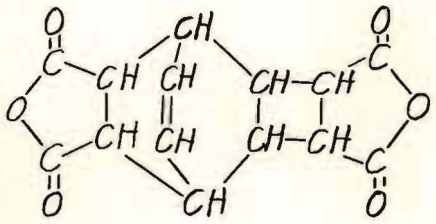
Angus and Bryce-Smith in a recent communication[2] have described the addition

(2) H. J. F. Angus and D. Bryce-Smith, Proc. Chem. Soc., (London), 326 (1959).

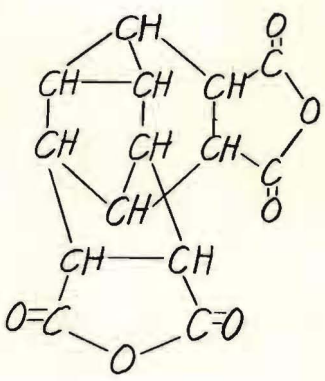
of maleic anhydride to benzene at 60° under the influence of ultraviolet radiation to give a product of m.p. 356° which they provisionally suggest has the structure (I). We have independently discovered this[3] same adduct and wish to report experiments

(3) Our discovery of the 2:1 adduct of maleic anhydride with benzene is contained in the M.S. thesis of J. W. Taylor, Georgia Institute of Technology, June, 1958, and was announced by E. G. at the Seventh Reaction Mechanisms Conference, University of Chicago, September 5, 1958, during the discussion of the paper of Prof. G. Buchi on light-catalyzed organic reactions.

which provide proof for the structure (I) proposed by Angus and Bryce-Smith and which moreover establish the likely stereochemical structure of the adduct.



I



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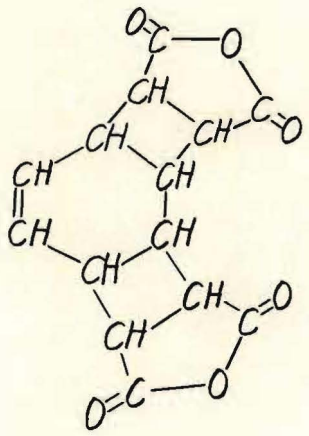

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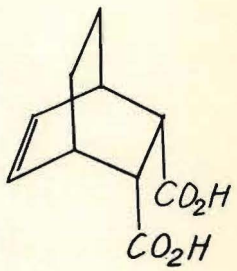
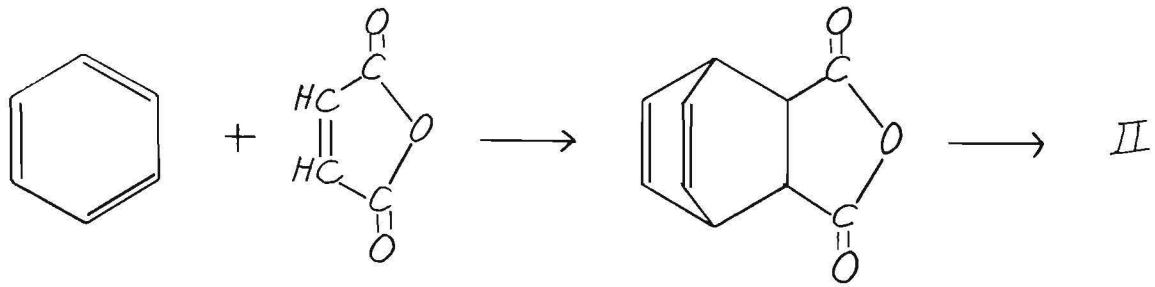


V

We have prepared the adduct in 13% yield (based on maleic anhydride) by irradiating for 16 hours with ultraviolet light a nearly saturated solution of maleic anhydride in benzene in a quartz apparatus at room temperature. Larger scale preparations of the adduct in the same apparatus were made in a mixed solvent of acetone and benzene in which maleic anhydride is some ten times more soluble than in benzene alone; acetone seems to have no adverse effect on the yield of product. The adduct is a white crystalline solid of m.p. 355-357° (dec.). It is somewhat soluble in acetone but is essentially insoluble in common organic solvents such as benzene and ether.

The adduct gave correct carbon-hydrogen analyses for $C_{14}H_{10}O_6$ and a saponification equivalent of 68.4 as expected for an adduct from one molecule of benzene combined with two molecules of maleic anhydride. Molecular weight determinations by the melting-point depression technique were unsuccessful in camphor, triphenylethane, β-naphthol, biphenyl or 2,4,6-tribromophenol apparently because the adduct is too insoluble in the melts from these compounds. However the adduct cannot likely have a molecular weight which is two-fold or more that of $C_{14}H_{10}O_6$ because the adduct can be sublimed with only slight decomposition at 240° and 0.02 mm. pressure. Moreover the adduct gives, upon refluxing with 0.08 M methanolic hydrogen chloride, a tetramethyl ester, m.p. 134.5-135.0°, which has correct carbon-hydrogen analyses and molecualr weight (in camphor) for $C_{18}H_{22}O_8$.

The tetracarboxylic acid obtained from saponification of the adduct had satisfactory carbon-hydrogen analyses for $C_{14}H_{14}O_8$ and decomposed at 125-200°, evidently with loss of water, and finally melted at 355-357°(dec.), which is the same as the melting point observed for the adduct anhydride. The acid upon hydrogenation in glacial acetic acid over a 5% platinum on carbon catalyst at room temperature and atmospheric pressure slowly absorbed over a 24-hour period one mole of hydrogen per mole of acid. The anhydride did not decolorize $KMnO_4$ in acetone and showed no reaction with bromine in boiling acetic acid under otherwise the usual conditions for these tests. Similarly, the methyl ester did not decolorize $KMnO_4$ in ethanol nor show any reaction with bromine in methanol in the dark, the latter even after six days. We were led on the basis of these tests for unsaturation to postulate[3] the presence of a cyclopropane ring in our adduct rather than a double bond. A simple structure for the adduct which contains a cyclopropane ring is structure II. This structure could be formed by 1,4-addition of one molecule of maleic anhydride to benzene to give IV and then 1,5-addition of a second molecule of the anhydride to give II:



IV II

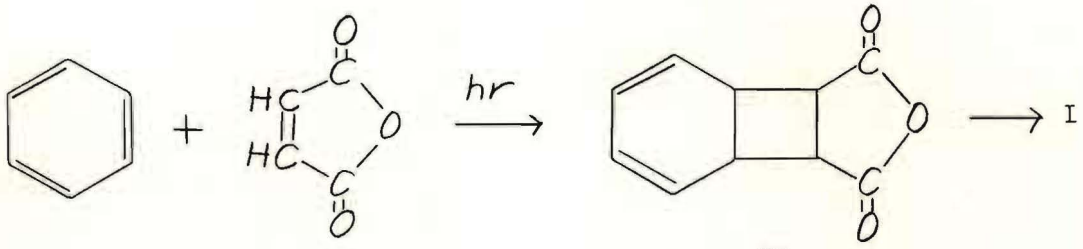
As an analogy for the reaction of IV with maleic anhydride to give II, the thermal addition of maleic anhydride to bicyclo[2,2,1]heptadiene[4] may be cited.

(4) E. F. Ullman, Chem. & Ind. (London), 1173 (1958).

In agreement with a structure such as II, the sodium salt of the tetracarboxylic acid shows no ultraviolet absorption maxima down to 210 mμ but does show "end-absorption" ($\epsilon_{220m\mu} \simeq 530$) much like that of the sodium salt of endo-cis-bicyclo[2,2,2]-5-octene-2,3-dicarboxylic acid[5] (V) ($\epsilon_{220m\mu}=390$).

(5) K. Alder and G. Stein, Ann., 514, 15 (1934).

Angus and Bryce-Smith[2] report for the tetracarboxylic acid (?) a weak absorption maximum at 265 mμ ($\epsilon=55$). These workers observed that per-acid titration of the tetramethyl ester indicated the presence of one ethylenic bond per molecule and, on the basis of this information and data rather similar to that given previously, suggested provisionally structure (I) for the adduct. They noted that structure (I) could reasonably be formed by 1,2-addition of one molecule of maleic anhydride to benzene to give VI followed by 1,4-addition of a second molecule of the anhydride to give I:



VI

We would note that VI could conceivably add a second molecule of maleic anhydride by 1,2-addition, rather than by 1,4-addition, to give III rather than I. Furthermore structures I, II, and III can exist in many different stereochemical forms. Finally in view of the known complexity of some photochemical reactions, there is no certainty that the principle of minimum chemical change is not violated in the photochemical reactions leading to the benzene-maleic anhydride adduct. Obviously more detailed studies are necessary to decide between the many possibilities.

The nuclear magnetic resonance spectrum of the tetramethyl ester of the benzene adduct in deuterochloroform shows the following proton chemical shifts[6],

(6) L. H. Meyer, A. Saika, and H. S. Gutowsky, This Journal, 75, 4567 (1953).

$\delta = 10^5$ (Hr-Hc)/Hr, measured relative to water at the relative intensities given in parentheses (expressed as number of hydrogen atoms): +0.16 (1.8); doublet at -0.13 (12.1); -0.195, -0.202, -0.24 (8.1). The first band is attributable to two ethylenic hydrogen atoms, though the absorption is nearer the value recorded[6] for tiglaldehyde or benzene than for cyclohexene. The band at -0.13 is in the region expected[6] for CH_3O and is of the correct intensity for four methoxyl groups; that this band is split into two bands of essentially equal intensity must mean that two of the methoxyl groups are in one type of environment and two are in an appreciably different environment (this cannot be ordinary spin-spin splitting because of the isolation of the hydrogen atoms of the carbomethoxyl groups from nearest neighboring hydrogen atoms by five or more intervening bonds). The last group of bands are not well resolved and appear near the region expected[7]

(7) K. L. Rinehardt, Jr., W. A. Nilsson, and H. A. Whaley, ibid., 80, 503 (1958).

for hydrogen on a carbon atom adjacent to a carboxyl or ethylenic group. It is significant that no absorption was found in the region expected for hydrogen on a cyclopropane ring[4,8]. The infrared spectrum of the adduct as the anhydride, the

(8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, N. Y., 1959, p. 236.

acid, or the methyl ester contains no absorption in the 6.73-6.92 μ region (frequency of CH_2 deformations[9]), while a band appears at 6.80 μ in the hydrogenated acid.

(9) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd. ed. Methuen & Co., Ltd., London, 1958, p. 13.

Since the nuclear magnetic resonance absorption spectrum of the tetramethyl ester of the benzene adduct strongly indicates the presence of an olefinic bond and the absence of a cyclopropane ring, the chemical evidence was examined in greater detail. While the sodium salt of the tetracarboxylic acid does not decolorize $KMnO_4$ in 5 minutes at room temperature, some decolorization occurs within a half hour. Similarly the tetracarboxylic acid in dilute hydrochloric acid solution slowly decolorizes bromine-water over a period of several hours. In sharp contrast, the sodium salt of the tetracarboxylic acid in aqueous solution reacts almost instantaneously with bromine to give, after acidification, a bromolactonic

acid which after reaction with excess diazomethane was isolated as a methyl ester VII, m.p. 215-216°. This compound had a satisfactory analysis for carbon, hydrogen, and bromine as calculated for the formula $C_{17}H_{19}BrO_8$ and therefore appears to be a trimethyl ester-bromolactone. This ester has infrared absorption at 5.63 and 5.80 μ near that expected [10] respectively for the carbonyl group of a gamma-lactone and of

(10) Ref. (9) p. 179.

a carbomethoxyl group. Moreover the sodium salt of the tetracarboxylic acid with aqueous I_2-KI solution absorbs in 72 hours at room temperature 9.7% or at 50° 70% of one mole of iodine per mole of acid. In comparative runs under similar conditions the sodium salt of endo-cis-bicyclo[2.2.2]-5-octene-2,3-dicarboxylic acid[5] (V) immediately decolorizes aqueous $KMnO_4$ and absorbs 97% of one molar equivalent of iodine in 23 seconds at room temperature (i.e., iodination occurs about a million times faster with the salt of IV than with the salt of the benzene-maleic anhydride adduct). In conclusion the chemical evidence shows that the benzene-maleic anhydride adduct has one rather highly hindered double bond. Structure II for the adduct can therefore be discarded on the basis of both the chemical data and the nuclear magnetic resonance absorption spectrum.

The tetramethyl ester of the adduct when heated at reflux in methanol containing a large excess of hydrazine gave a 85% yield of a product of m.p. 218-219° (dec.) which gave a fair analysis for a dihydrazide, $C_{16}H_{22}O_6N_4$. The dihydrazide when distilled at 0.01 mm. lost hydrazine and gave a cyclic hydrazide of m.p. 204.7-205.7° which gave a good analysis for $C_{16}H_{18}O_6N_2$. The cyclic hydrozide when heated at reflux in methanol containing a large excess of hydrazine deposited crystals (87% yield) of the starting dihydrazide. As judged by the behavior of the tetramethyl ester with hydrazine, two of the carbomethoxyl groups are considerably more readily attacked by hydrazine than the other two, and these reactive carbomethoxyl groups must be part of the same maleic acid radical since the dihydrazide may be pyrolyzed to a cyclic hydrazide. The chemical evidence, therefore, supports the nuclear magnetic resonance absorption data in indicating that two of the carbomethoxyl groups of the tetramethyl ester are in an appreciably different environment than the other two carbomethoxyl groups. These data render structure III improbable in any of its likely stereochemical forms either because its double bond should be readily attacked by $KMnO_4$ or because it has two maleic anhydride radicals in equivalent positions. Of the structures for the benzene-maleic anhydride adduct which are in accord with the principle of minimum structural change, we are left with structure I as the most probable structure.

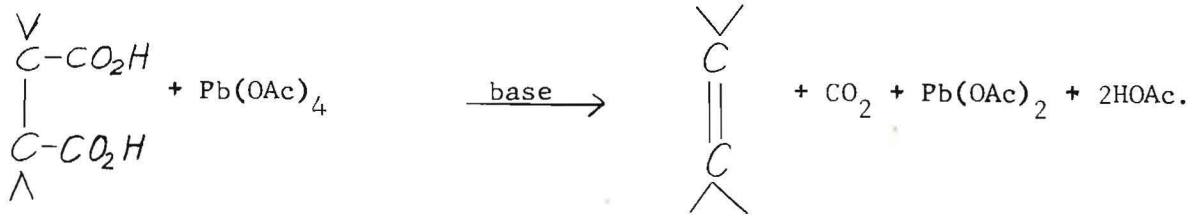
Much more conclusive evidence for the structure of the adduct has been provided by oxidation[11] of a pyridine solution of the tetracarboxylic acid or better the

(11) We are indebted to Mr. Gary G. Hammer and Dr. Leon H. Zalkow for pointing out to us the method of Grab and co-workers and to Dr. Jack Hine for suggesting the use of pyridine as a solvent for this reaction.

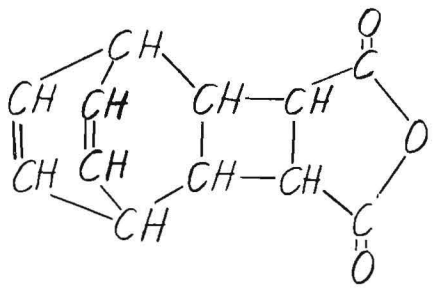
the adduct anhydride itself with lead tetraacetate. Grob[12] and co-workers have reported

(12) C. A. Grob, M. Ohta, and A. Weiss, Angew. Chem., 70, 343 (1958).

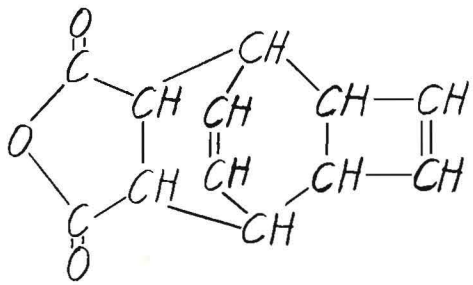
that oxidation of several cis-1,2-dicarboxylic acids in presence of one to two molar equivalents of a base such as pyridine in benzene or acetonitrile as solvent gave 50-70% yield of olefin in accord with the process:



From oxidation of the benzene-maleic anhydride adduct with lead tetraacetate in pyridine at 50 to 62°, 56% yield was obtained of a product of m.p. 167-168.7° which had satisfactory analysis for $C_{12}H_{10}O_3$. The same product, but in lower yield, was obtained by oxidation of the tetracarboxylic acid. During the lead tetraacetate oxidation, therefore, only one of the two maleic anhydride radicals of the adduct was oxidized. On the basis of structure I for the adduct, the lead tetraacetate oxidation could give either VIII or IX for the product of composition $C_{12}H_{10}O_3$. Structure IX can exist in four stereochemical forms (involving cis-fusion of the four-and five-



VIII



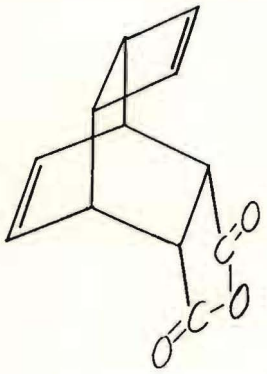
IX

membered rings to the[2.2.2] bicyclooctene system), one of these forms corresponds to the known[13] maleic anhydride adduct of cyclooctatetraene. It is remarkable,

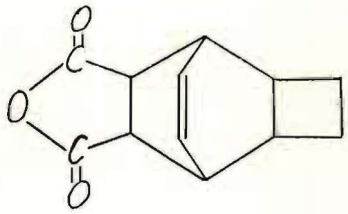
(13) (a) W. Reppe, O. Schlichting, K. Klager, and T. Toeppel, Ann., 560, 1 (1948); (b) A. C. Cope and C. G. Overberger, This Journal, 70, 1433 (1948).

therefore, that the product $C_{12}H_{10}O_3$ from lead tetraacetate oxidation of the benzene-maleic anhydride adduct was found to be identical (mixed m.p. and infrared spectral comparisons) with the maleic anhydride adduct of cyclooctatetraene. This evidence conclusively establishes the structure of the benzene-maleic anhydride adduct as I in agreement with the brilliant provisional suggestions of Angus and Bryce-Smith[2]. There remains unanswered the question of the stereochemical structure of the photochemical adduct.

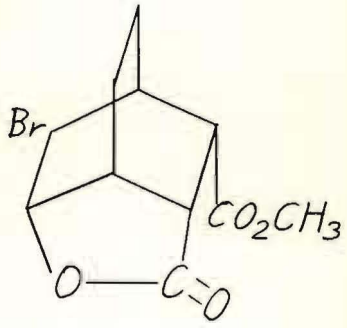
Structure I can exist in eight possible stereoisomeric forms with cis-fusion of the maleic anhydride groups. A key to the stereochemical form of the benzene-maleic anhydride adduct is found in the stereochemistry of the cyclooctatetraene-maleic anhydride adduct IX. Reppe[13a] and co-workers reported that this adduct gives a bromolactonic acid; therefore, the carboxyl groups of the adduct must be located in close proximity to one of the double bonds of the adduct. These workers have proposed that the cyclooctatetraene-maleic anhydride adduct has the stereochemical formula X and, therefore, that bromolactone formation involves attack of bromine



X



XI



XII

on the double bond in the six-membered ring to give a γ-lactone. Cope[14] and co-workers

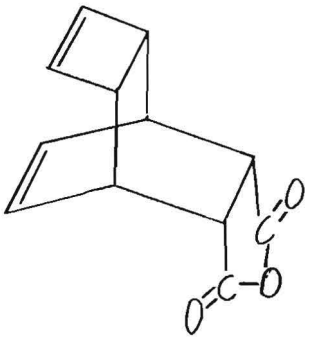
(14) A. C. Cope, A. C. Haven, Jr., F. L. Ramp, and E. R. Trumbull, ibid., 74, 4867 (1952).

have proven that hydrogenation of the cyclooctatetraene-maleic anhydride adduct under mild conditions adds a mole of hydrogen to the double bond of the four-membered ring to give XI rather than to the double bond of the six-membered ring as previously supposed[13a]. Hence Cope et al. have pointed out that bromolactone formation may involve addition of bromine to the double bond of the four-membered ring; if this is the case, the bromolactone of IX is a delta-lactone. To distinguish between these possibilities we have examined the infrared absorption spectrum of the mono-methyl ester[13a] of the bromolactone of IX. This compound has carbonyl absorption at 5.69 and 5.76 μ. The first value agrees somewhat more closely with the absorption expected[10] for a γ-lactone (5.62-5.68 μ) than that for a δ-lactone (5.71-5.76 μ), while the second value corresponds to the value expected for the carbonyl groups of an ester. We find that the bromolactonic ester XII of endo-cis-bicyclo[2.2.2]-5-octene-2,3-dicarboxylic acid[5] (V) has carbonyl absorption at 5.69 amd 5.79 μ; hence γ-lactones in polycyclic systems may give carbonyl absorption at 5.69 μ as found for the cyclooctatetraene adduct.

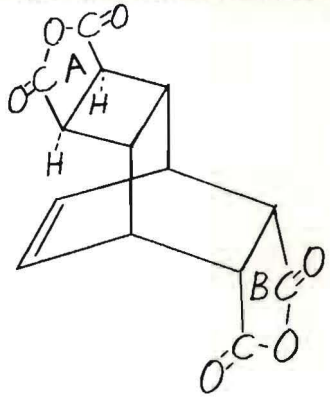
To provide more conclusive proof of the stereochemistry of IX, the reaction of the dihydro derivative XI with bromine has been investigated. Of the four possible stereoisomers of IX with cis orientation of the carbonyl groups, it may be seen that the carbonyl groups of the corresponding acid may be oriented near one or the other or none of the double bonds but cannot be oriented for a particular isomer such that bromolactone formation can take place with either double bond. Hence one method for determining which double bond is oriented near to the carbonyl groups is to remove one double bond by hydrogenation and see if the corresponding dihydro-derivative can form a bromolactone. Cope and co-workers evidently had this strategy in mind when they reported[14] that dihydro-derivative XI "does not react readily with bromine", but did not specify the conditions tried. Because of our previous experience in bromination of the benzene-maleic anhydride adduct (see earlier discussion), we were led to reinvestigate the bromination of XI. While XI did not decolorize a solution of bromine in CCl_4 or acetic acid in 3 hours the potassium salt of XI in water reacted almost instantaneously with one molar equivalent of bromine to give a good yield of a crystalline product of m.p. 243-244°(dec.), which had the expected composition for a bromolactonic acid, $C_{12}H_{13}O_4Br$. The corresponding crystalline mono-methyl ester, $C_{13}H_{15}O_4Br$, had carbonyl absorption at 5.65 and 5.77 μ as expected for the methyl ester of a γ-lactone. Hence the carbonyl groups of IX are oriented near to the double bond in the six-membered ring rather than near the double bond of the four-membered ring. Thus structure X of Reppe[13a] et al. is correct in so

far as this particular structural detail is concerned.

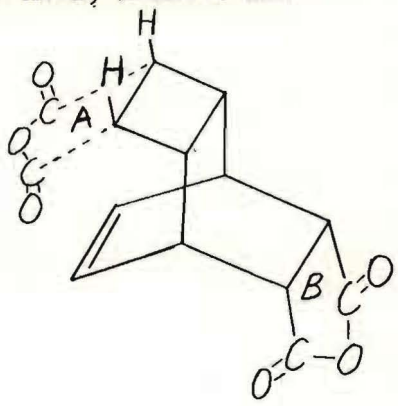
There was never, however, any compelling evidence for the steric orientation of the four-membered ring of X relative to the cyclohexene ring. Structure XIII would appear to be equally probable and has been written by Abel, Bennett and



XIII



XIV



XV

Wilkinson[15]. These workers have found that the cyclooctatetraene-maleic anhydride

(15) E. W. Abel, M. A. Bennett and G. Wilkinson, J. Chem. Soc., 3178 (1959).

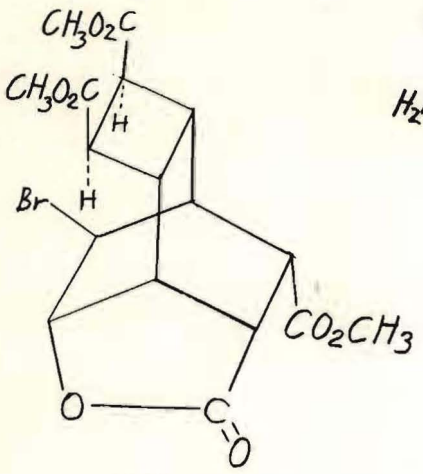
adduct forms a crystalline rhodium(I) chloride complex which is believed to involve chelation by the diolefin group to one rhodium atom. The two double bonds in the cyclooctatetraene-maleic anhydride adduct are, therefore, almost certainly oriented as in XIII especially since bicyclo [2.2.1]-heptadiene (norbornadiene) forms a similar rhodium(I) chloride complex[15].

If no changes in steric orientation of groups occur during the oxidation of the benzene-maleic anhydride adduct (I) by lead tetraacetate to give XIII, then only structures XIV and XV need by considered for the photochemical adduct. No changes in stereochemistry are expected to occur during the lead tetraacetate oxidation because of the mild conditions of the reaction and the speed of the oxidative decarboxylation. These expectations appear to be confirmed since the tetracarboxylic acid of I gave XIII as only insoluble acidic product while at least some of the trans-acid[13a] would have been expected if any isomerization had occured at the centers bearing the carboxyl groups. Furthermore the photochemical adduct I gave a bromo-γ-lactone and hence one acid anhydride group in I must be oriented as in XIII. Of the two structures XIV and XV, structure XIV appears much more probable than XV. The location of anhydride group A as in XIV rather than as XV is implied

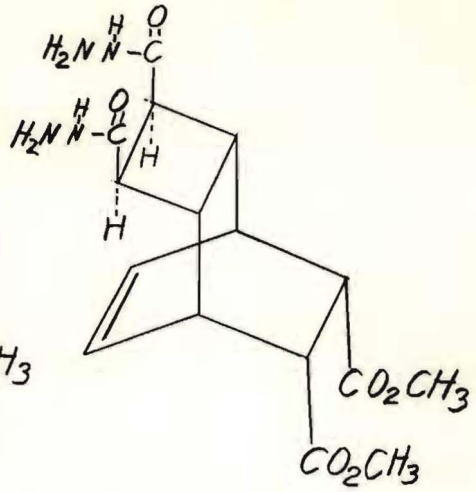
from the observations: (1) hydrazine readily attacks only two adjacent carbomethoxyl groups of the corresponding tetramethyl ester, (2) lead tetraacetate oxidation removes the two carbonyl groups of anhydride group A and hence these are implicated as the less hindered carbonyl groups, (3) the alternative location of the carbonyl groups A as in XV would place these goups very close to the double bonds and models indicate that the carbonyl groups A would then be more hindered than the carbonyl groups B, (4) bromolactone formation gives a γ-lactone as expected from XIV while a δ-lactone might be expected from XV.

In conclusion structure XIV is assigned as the probable stereochemical structure of the photochemical adduct of benzene with maleic anhydride. This structure contains a double bond which is hindered on either side from the approach of external reagents. Structure XIV, therefore, accounts for the remarkable unreactivity of the double bond toward permanganate and halogens. The structures of some of the other compounds prepared in the present work are summarized in Chart 1 and certain of these structural assignments are discussed in the Experimental Details.

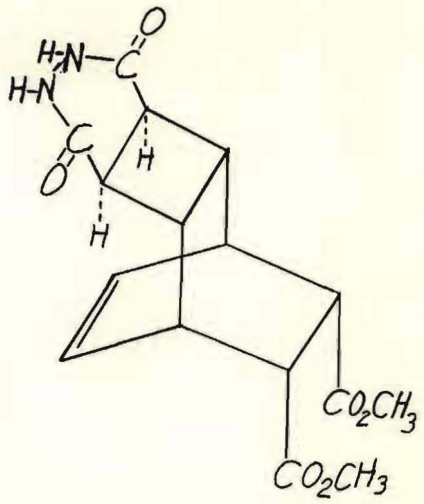
CHART 1



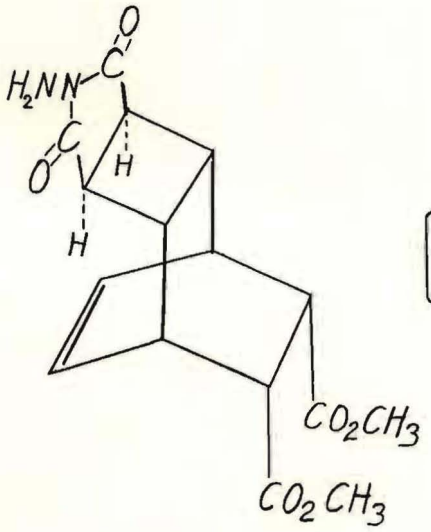
VII



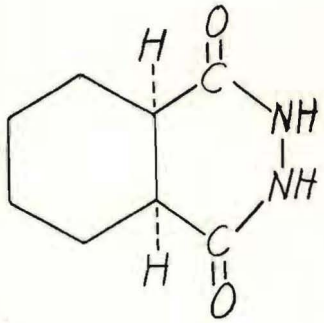
XVI



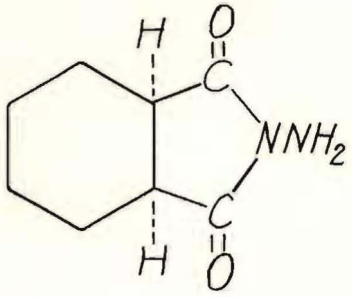
XVIIa



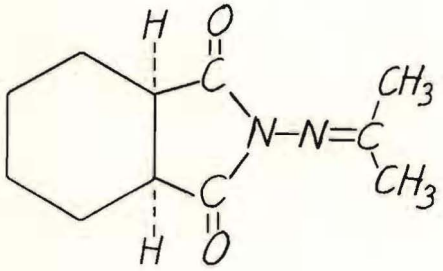
XVIIb



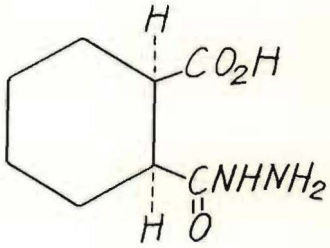
XVIIIa



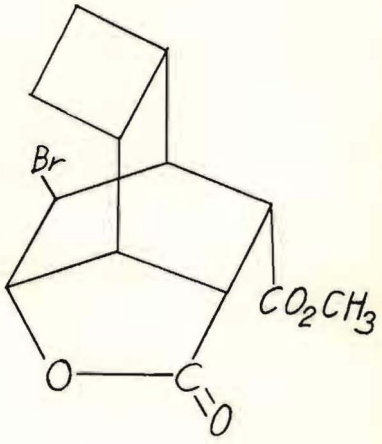
XVIIIb



XIX



XX



XXI

Experimental Details[16]

(16) All melting points are corrected. Analyses are by Clark and Galbraith Microchemical Laboratories.

Benzene-Maleic Anhydride Adduct (XIV).—Maleic anhydride (10.0 g., 0.102 moles) was dissolved in 300 ml. of thiophene-free benzene. The solution was placed in a water-cooled quartz cell which encircled a 1000-watt Hanovia mercury-arc lamp[17].

(17) For a more detailed description of the apparatus see E. Grovenstein,Jr., and S. P. Theophilou, This Journal, 77, 3795 (1955).

The solution was irradiated for 16 hours. During this time white crystals precipitated on the walls of the cell. The precipitate of XIV was separated by filtration and washed with three 25 ml. portions of boiling benzene. The yield of XIV was 1.90 g. or 13.6% of product of m.p. 355-357° (dec).

For larger scale preparations 118 g. (1.20 moles) of freshly distilled maleic anhydride was dissolved in 100 ml. of acetone (which had been purified by distillation from $KMnO_4$) and 125 ml.(1.4 moles) of thiophene-free benzene was added. The solution after irradiation in the apparatus described above for 25 hours deposited 10.5 g. of adduct which was separated by filtration. Another 6.5 g. of adduct was recovered by evaporation of the solvent, boiling the residue with about 200 ml. of acetone to dissolve unreacted maleic anhydride, and separation of the adduct by filtration. The yield of product (17.0 g.) was 10.3 %. In similar runs with 120 g. of maleic anhydride and an irradiation time of 48 hours 16.0 to 18.0 g. of adduct deposited in the cell but only some 1.5 g. of additional adduct was recoverable from the reaction solution.

The adduct when thoroughly washed with hot benzene or acetone did not decolorize dilute solutions of $KMnO_4$ in acetone; however, maleic anhydride readily decolorizes such $KMnO_4$ solutions and thus the permanganate test is a convenient test for the purity of the adduct from the present preparations. The adduct sublimed slowly at 0.015 mm. and a bath temperature of 240-250° to give a product of m.p. 355-357° (dec.), while at higher temperatures a brown product was obtained.

Anal. Found: C, 61.24, 61.37; H, 3.64, 3.74; saponification equiv., 68.4. Calcd. for $C_{14}H_{10}O_6$: C, 61.32; H, 3.68; saponification equiv. for tetrabasic acid anhydride, 68.55.

Tetramethyl Ester of XIV.— The benzene-maleic anhydride adduct (1.80 g.) was esterfied by boiling under reflux with anhydrous methanol (100 ml.), which was 0.078 M in anhydrous hydrogen chloride, for six hours. The solution was concentrated to 20 ml. and, on cooling, 1.58 g. of white crystals, m.p. 130-132°, precipitated. Recrystallization three times from anhydrous methanol gave methyl ester of m.p. 134.5-135.0°. This product sublimed readily at a bath temperature of 200° and a pressure of 0.015 mm.

Anal. Found: C, 58.82, 58.91; H, 5.88, 5.89; mol. wt., 366 (determined in camphor, with triphenylmethane used to determine the melting-point depression constant). Calcd. for $C_{18}H_{22}O_8$: C, 59.01; H, 6.05; mol. wt., 366.4

The tetracarboxylic acid of XIV (see below) upon esterification with methanolic hydrogen chloride by a rather similar procedure gave a methyl ester of m.p. 133.0-133.4° which showed no m.p. depression with the methyl ester prepared from the anhydride and, moreover, had an identical infrared absorption spectrum.

Tetracarboxylic Acid of XIV.— The benzene-maleic anhydride adduct (25.5 g., 0.0929 mole) was heated at reflux with 254 ml. of 1.46 M aqueous KOH (0.372 mole) with occasional shaking for 5 hours. The solution was cooled and filtered to remove a small amount of suspended solid. The solution upon acidification with hydrochloric acid yielded a fine crystalline precipitate. The precipitate was separated and recrystallized from water to give 20.0 g. of crystals. After two additional crystallizations from water, the product showed decomposition at 125-200° ($-H_2O$) and finally melted at 350-353° (dec.). The analytical sample was recrystallized two more times from water and had m.p. 356-357° (dec.) with previous loss of water near 120°.

Anal. Found: C, 54.46, 54.69; H, 4.16, 4.21. Calcd. for $C_{14}H_{14}O_8$: C, 54.20; H, 4.55.

The tetracarboxylic acid (0.553 g.) in 80 ml. of glacial acetic acid was hydrogenated at room temperature over 0.49 g. of a 5% Pt on charcoal catalyst. After 24 hours the sample had absorbed 36.9 ml. (S.T.P.) of hydrogen or 0.925 mole of hydrogen per mole of acid taken. No more hydrogen was absorbed in an additional 72 hours. An analysis of the particular sample of tetracarboxylic acid taken

gave: C, 49.99; H, 4.38; ash, 7.4. After correction for ash, the analytical data became C, 53.98; H, 4.73; 1.00 mole of hydrogen absorbed per mole of acid. From the hydrogenation mixture an acid of m.p. 295-297° (dec.) was isolated; this dihydro acid was considerably more soluble in acetic acid than the starting acid and was converted into an acid anhydride upon heating with acetic anhydride.

Bromolactone Trimethyl Ester (VII) of XIV. — The tetracarboxylic acid of XIV, 1.52 g. or 4.9 mmoles, was dissolved in about 20 ml. of aqueous sodium hydroxide and the excess of base was neutralized with hydrochloric acid to pH 9. Bromine was added slowly with shaking until a pale yellow color of bromine remained (0.24 ± .02 ml. of bromine added or some 4.7 mmoles). The bromine color was almost instantaneously discharged at first but near the end of the addition the color remained a short while. The solution was acidified with 10 ml. of concentrated hydrochloric acid and evaporated to dryness in the steam bath. The residue was ground up and extracted several times with, in all, 55 ml. of tetrahydrofuran. A solution of diazomethane in ether was added to the tetrahydrofuran solution until a yellow color persisted. Evaporation of the solvents gave white crystals which were partially dissolved by 125 ml. of hot methanol. Filtration of the cooled solution gave 1.07 g. of white crystals of m.p. 211-215°. After two crystallizations from benzene the product had m.p. 215.0-216.3°.

Anal. Found: C, 47.11, 47.19; H, 4.35, 4.41; Br, 18.52, 18.59. Calcd. for $C_{17}H_{19}BrO_8$: C, 47.34; H, 4.44; Br, 18.53.

Iodolactone Formation by XIV and V. — The sodium salts of the anhydrides of XIV and V were prepared by heating the anhydride with some 30% excess sodium hydride solution and back-titration with hydrochloric acid almost to the disappearance of the color of phenolphthalein. For iodolactone formation one volume of the sodium salt of XIV or V was mixed with an equal volume of iodine-potassium iodide solution to give an initial solution which was 0.018 M in the salt of XIV or V, 0.025 M in iodine, and 0.137 M in sodium iodide. For measurement of the consumption of iodine, slow iodinations were acidified with acetic acid and titrated with thiosulfate to a starch end-point, while fast reactions were made strongly acidic with hydrochloric acid before titration of unreacted iodine.

Reaction of Tetramethyl Ester of XIV with Hydrazine. — The tetramethyl ester of XIV (2.00 g.) was heated at reflux with 5.0 ml. of 98% hydrazine in 25 ml. of methanol for two hours. A white precipitate separated during the reaction and after separation by filtration from the cold reaction mixture amounted to 1.70 g. (85% yield) of compound of m.p. 218 - 219° (dec.). This compound XVI appears

to be a dihydrazide dimethyl ester of XIV and was found to be identical (mixed m.p. and infrared spectral comparisons) with the compound of similar m.p. prepared below by reaction of hydrazine with the cylic hydrazide XVII. Compound XVI was soluble in water and acetic acid but was essentially insoluble in solvents such as benzene and methyl alcohol. Since attempts to recrystallize XVI from common solvents were unsuccessful, a 1.3 g. sample of XVI was subjected to vacuum sublimation at 0.01 mm. and a bath temperature of 270°. Sublimation was complete in 0.5 hrs. The sublimate was taken up in 25 ml. of hot methanol. The solution was filtered to remove a small amount of insoluble material and on cooling deposited white crystals. After two recrystallizations from methanol the product amounted to 1.0 g. of material of m.p. 202.7-203.7°. The analytical sample was recrystallized two more times from methanol and sublimed four times (at 240° and 0.01 mm.) to give cyclic hydrazide XVII (structure XVIIa or XVIIb) of m.p. 204.7-205.7°.

Anal. Found: C, 57.65; H, 5.55; N, 8.32. Calcd. for $C_{16}H_{18}O_6N_2$: C, 57.48; H, 5.43; N, 8.38.

Compound XVII (0.50 g.) was dissolved in 25 ml. of methanol. To the solution was added 2.0 ml. of 98% hydrazine and the mixture was heated at reflux for 1.5 hr. during which time a white precipitate appeared. Filtration of the cooled solution gave 0.48 g. (87% yield) of white crystals of XVI of m.p. 218-219° (dec.)[18].

Anal. Found: C, 51.80; H, 6.01; N, 15.36. Calcd. for $C_{16}H_{22}O_6N_4$: C, 52.45; H, 6.05; N, 15.29.

The tetramethyl ester of XIV (2.0 g.) was heated at reflux with 5.0 ml. of 98% hydrazine for 15 min. Methanol (20 ml.) was added and the reaction mixture was heated at reflux for 3 hrs. The dull white solid which separated amounted to 1.6 g. The product was boiled with 10 ml. of absolute methanol and on separation by filtration was a pure white solid of m.p. 211-213° (dec.). The material did not sublime or distill at temperatures up to 300° at 0.015 mm. and and may therefore be a polymer. The product had almost as much nitrogen as expected for the tetrahydrazide of XIV.

Anal. Found: N, 28.30. Calcd. for $C_{15}H_{22}O_5N_6$: N, 22.94; calcd. for $C_{14}H_{22}O_4N_8$: 30.59.

The reaction of the dimethyl ester of cis-hexahydrophthalic acid with hydrazine was studied as a model to aid in understanding the reactions of the tetramethyl ester of XIV with hydrazine.

Cyclic Hydrazide XVIII of cis-Cyclohexane-1,2-dicarboxylic Acid.-Dimethyl cis-cyclohexane-1,2-dicarboxylate (5.0 g.) was heated with 5.0 ml. of 98% hydrazine at

reflux for 15 min. Just enough methanol was added to give a homogeneous solution and the mixture was heated at reflux for one hour. Concentration of the solution gave a crystalline product which, after one recrystallization from 85% methanol, amounted to 4.8 g. of dihydrazide of m.p. 229-230° (dec.) (recorded: trans[18a], 229-31°; cis[18a], 123-4.5° and then 228.5-229.5°; unspecified isomer [18b], 245°). The

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(18)(a) V. G. Iashunskii, J. Gen. Chem. U.S.S.R. (Eng. Transl.), 28, 1420 (1958); (b) H. Wieland, O. Schlichting, W. v. Langsdorff, Z. physiol. Chem., Hoppe-Seyler's, 161, 78 (1926). The m.p. of our dihydrazide of cyclohexane-1,2-dicarboxylic acid was variable with the rate of heating. At a fast rate of heating the m.p. was some 15° higher than the value reported above. Similar observations were made with respect to the m.p. of dihydrazide XVI.

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dihydrazide (45 g.)from a similar large-scale preparation was pyrolyzed at a bath temperature of 280-290° and a pressure of 20 mm. to give distillate of b.p. 220-230° at 20 mm. The distillate (30 g.) solidified on cooling and had m.p. 55-60°. A second distillation gave a colorless product of b.p. 152-160° at 0.5 mm. and of m.p. 60-63°. Redistillation through a short fractionating column gave cyclic hydrazide XVIII of m.p. 60.4-62.9°.

Anal. Found: C, 57.42; H, 7.02; N, 16.42, Calcd. for $C_8H_{12}O_2N_2$: C, 57.13; H, 7.19; N, 16.66.

The cyclic hydrazide XVIII (3.0 g.) was dissolved in 30 ml. of concentrated hydrochloric acid and the mixture heated at reflux for 15 minutes. The solid which precipitated was separated by filtration of the cool solution and was washed with water. The product (2.6 g.) had m.p. 187.3-188.7° as expected for cis-cyclohexane-dicarboxylic acid (recorded[18a], m.p. 189.5-190.5°). Similar treatment of our starting dihydrazide of cyclohexane-1,2-dicarboxylic acid (3.0 g.) with 30 ml. of concentrated hydrochloric at reflux for 30 minutes gave 1.3 g. of product of m.p. 182-204°. This product upon sodium fusion gave a negative test for nitrogen and halogen and thus appears to be a mixture of cis- and trans-cyclohexane-1,2-dicarboxylic acids.

For an attempted purification by recrystallization, XVIII was dissolved in a minimum amount of acetone and two volumes of n-hexane was added. The mixture was heated on a steam bath and the supernatant hexane layer was separated. Two similar hexane extractions were made and from the combined hexane extracts crystals in the form of needles were obtained on cooling. These after another similar crystallization from acetone-n-hexane had m.p. 124.0-125.5° (with previous sintering at 120°).

Anal. Found: C, 63.89; H, 7.98; N, 13.12. Calcd. for $C_{11}H_{16}O_2N_2$: C, 63.44; H, 7.74; N, 13.45.

This product has an analysis corresponding to that of an isopropylidene derivative of XVIII. The only likely structure for the isopropylidene derivative appears to be XIX. The ready formation of XIX from XVIII suggests that XVIII has structure XVIIIb rather than the isomeric structure XVIIIa. However, since Drew and Hatt[19] have shown that the more stable phthalhydrazide gives the same

(19) H. D. K. Drew and H. H. Hatt, J. Chem. Soc., 16 (1937).

benzylidine derivative as the less stable N-aminophthalimide though under more vigorous conditions, the reaction of XVIII with acetone cannot be regarded as affording proof of structure XVIIIb.

The potentiometric titration of succinhydrazide as a monobasic acid has been cited[20] as evidence in favor of the hydrazide structure as opposed to the N-amino-

(20) H. Feuer, G. B. Bachman, and E. H. White, This Journal, 73, 4716 (1951).

succinimide structure. We find that XVIII, when dissolved in excess sodium hydroxide and back-titrated potentiometrically with hydrochloric acid, gives a neutralization equivalent of 172 (theory for monobasic acid $C_8H_{12}O_2N_2$, 168). The direct titration of XVIII with sodium hydroxide is difficult since XVIII combines rather slowly with the base and our titrimetric data indicate that XVIII undergoes hydrolysis to give the salt of XX under the conditions of the titration. Since either XVIIIa or XVIIIb might be expected to undergo ready hydrolysis to XX, the titration is also unable to distinguish between the two likely structures for XVIII.

Oxidation of XIV with Lead Tetraacetate.- The anhydride XIV (5.0 g., 0.0182 mole) was dissolved in 200 ml. of hot pyridine (which had been dried over KOH pellets and freshly distilled). Lead tetraacetate (9.0 g., 0.020 mole) was added and the pyridine solution was maintained at 70-80° for one hour. During the first five minutes of reaction there was a vigorous evolution of carbon dioxide. The solvent was removed in vacuo with aid of a steam bath. The dark brown residue was acidified with hydrochloric acid and extracted with ether three times. The etheral extracts were combined, washed with water twice, and dried over anhydrous $MgSO_4$. After removal of the ether, 1.5 g. of crystalline product was obtained. This was sublimed at 0.025 mm. at a bath temperature of 170° to give 1.45 g. (39.5% yield) of crystalline sublimate. After two recrystallizations from chlorobenzene the product XIII had m.p. 166.9-168.7.

Anal. Found: C, 70.89, 70.92; H, 4.80, 4.95. Calcd. for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98.

A sample of the maleic anhydride addition product of cyclooctatetraene was prepared[13] by heating maleic anhydride with cyclooctatetraene under a nitrogen atmosphere at a bath temperature of 180° for 30 min. The product after sublimation in vacuo and recrystallization from chlorobenzene had m.p. 167.3-168.7° and gave no depression of m.p. when mixed with the product from the lead tetraacetate oxidation. Likewise the two products had identical infrared spectra.

A higher yield was obtained from reaction of 2.40 g. (0.00875 mole) of the anhydride XIV with 5.8 g. (0.013 mole) of lead tetraacetate in 85 ml. of pyridine maintained at 50-60° for one hour. The reaction mixture after standing over night was worked up as previously. After one sublimation in vacuo , the product amounted to 1.00 g. (56% yield) of material of m.p. 166.6-168.3°. A similar oxidation with lead tetraacetate in which 2 moles of lead tetraacetate were used per mole of anhydride gave only 34% yield of XIII.

Oxidation of the tetracarboxylic acid of XIV with lead tetraacetate was hindered, at least in part, by the low solubility of the acid in pyridine. Tetracarboxylic acid (5.0 g., 0.0161 mole) did not dissolve very completely in 150 ml. of boiling pyridine. To the mixture at 95-100° was added 10.0 g. (0.023 mole) of lead tetraacetate and the reaction mixture was kept at this temperature for one hour. The reaction was worked up as with the anhydride. From the ether extracts 0.50 g. of crude product was obtained. After one recrystallization from methanol the product amounted to 0.35 g. of material of m.p. 160-161.5°. Another recrystallization from methanol gave a product XIII of m.p. 167.1-167.9° which was identical with the maleic anhydride adduct of cyclooctatetraene (mixed m.p. and infrared-spectral comparisons).

Bromolactone of XI. -The dihydro derivative[14] of the maleic anhydride adduct of cyclooctatetraene (XI), 2.00 g. (0.0098 mole) of m.p. 142.5-143.5°, was dissolved in a warm solution of 3 g. of KOH in 50 ml. of water and the solution was filtered to remove a trace of suspended material. The solution was neutralized to a phenolphthalein end-point with hydrochloric acid and bromine was added dropwise with shaking. The color of bromine disappeared rapidly during addition of 0.45 ml. (8.8 mmoles) but a permanent yellow color remained after addition of 0.05 ml. (1.0 mmole) more bromine. Acidification gave a precipitate which after separation by filtration and recrystallization from 95% ethanol amounted to 2.50 g. (85% yield) of bromolactonic acid of m.p. 243.3-243.8° (dec.).

Anal. Found: C, 47.73, 47.81; H, 4.52, 4.40; Br, 26.61. Calcd. for $C_{12}H_{13}O_4Br$: C, 47.86; H, 4.35; Br, 26.54.

The bromolactonic acid was dissolved in tetrahydrofuran and a solution of diazomethane in ethyl ether was added until a pale yellow color persisted. The solvents were removed by evaporation and the resulting crystalline residue was recrystallized twice from methanol to give methyl ester XXI of m.p. 166.9 -167.9°.

Anal. Found: C, 49.45, 49.63; H, 4.80, 4.96; Br, 25.25. Calcd. for $C_{13}H_{15}O_4Br$: C, 49.54, H, 4.80; Br, 25.35.

Spectra.- Infrared spectra were run with samples in potassium bromide disks on a Perkin-Elmer model 21 infrared spectrometer with rock-salt prisms. Ultraviolet spectra were determined on a Beckman model DK-1 quartz spectrophotometer. The nuclear magnetic resonance absorption spectrum was determined on a Varian frequency R-F unit model V4310C with frequency of 40 megacycles and a field of 10,000 gauss. The tetramethyl ester of XIV (0.1 g.) was dissolved in 0.3 ml. of $DCCl_3$ and the chemical shifts were determined relative to $HCCl_3$ which was contained within an inner concentric tube. For calculations of chemical shifts relative to water chloroform was taken to have a chemical shift of 96 cycles/sec. at 40 Mc.

Acknowledgement.-We are indebted to Dr. Leon Mandell for the nuclear magentic resonance spectrum.

Part II

A Preliminary Search for Reaction of Maleic Anhydride with Thiophene, Chlorobenzene, Toluene, p-Xylene, and Naphthalene under Irradiation by Ultraviolet Light

SUMMARY

Maleic anhydride was found to undergo reaction with thiophene, chlorobenzene, toluene, and p-xylene when irradiated by ultraviolet light at room temperature. No product, however, was isolable from the corresponding attempted reaction of maleic anhydride with naphthalene. While mixtures of products appear to be obtained in all cases, the product from toluene was found to consist of some 67% of benzylsuccinic anhydride while that from p-xylene was at least 50% by weight of p-methylbenzylsuccinic anhydride.

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In order to investigate the scope of the scope of the photochemically activated reaction of maleic anhydride with benzene (see Part I), a preliminary investigation has been made to determine if photochemically activated reactions of maleic anhydride occur with thiophene, chlorobenzene, toluene, p-xylene, and naphthalene

With thiophene only 0.2 g. of dark brown acidic material was obtained. This product could be distilled in vacuo and contained sulfur. It therefore appears to be a reasonably low molecular weight product(s) of thiophene combined with maleic anhydride.

With chlorobenzene 1.0 g. of product was obtained of which 0.67 g. was an orange to brown solid. This material contained chlorine and was acidic in so far as tested. An attempted sublimation of the solid portion in vacuo resulted in decomposition. Thus chlorobenzene and maleic anhydride combine under influences of ultraviolet light to give a fair yield of product.

With toluene as much as 9.8 g. of liquid products were obtained. Hydrolysis of the product afforded benzylsuccinic acid in yields as high as 67% by weight of the total acidic product. Gas chromatography of the methyl esters of the crude product showed that as many as eight components may be present. The peroxide catalyzed addition of toluene to maleic anhydride has been reported[1] to give benzylsuccinic acid and it has been stated, but without any detail, that such reactions are catalyzed by ultraviolet light.

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(1) W. G. Bickford, G. S. Fischer, F. G. Dollear, and C. E. Swift, J. Am. Oil Chemist's Soc., 25, 251 (1948).

Since the reaction leading to benzylsuccinic acid evidently is a free-radical process[1], irradiation experiments were performed on a solution of maleic anhydride in toluene containing a little hydroquinone in order to inhibit the formation of benzylsuccinic anhydride. From such a reaction run under an atmosphere of nitrogen only 1.39 g. of product was obtained, but some 40% or more of the product was still benzylsuccinic anhydride.

With p-xylene and maleic anhydride, irradiation was ultraviolet light again led to a high conversion of products of which at least 50% was p-methylbenzylsuccinic anhydride. Doubtlessly other products are formed here as well, but they have not been characterized. The peroxide catalyzed reaction of p-xylene with maleic anhydride has been reported to yield p-methylbenzylsuccinic anhydride[2].

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(2) H. Schecter and H. C. Barker, J. Org. Chem., 21, 1473 (1956).

With naphthalene maleic anhydride was found to undergo no detectable photochemical reaction. Under the conditions investigated there was a recovery of 97.8% of the starting naphthalene.

After the preliminary experiments recorded here were completed[3], Schenck and Steinmetz[4] reported that benzophenone acts as a photosensitizer for the reaction of maleic anhydride with benzene, toluene, o-xylene, and chlorobenzene. In each case the products are formed from combination of two moles of maleic anhydride with one mole of the aromatic compound. The product from benzene is identical with that produced in absence of the photosensitizer.

(3) See our status reports number 2, 3, and 4 for work done in the period April 1, 1959 through December 31, 1959.

(4) G. O. Schenck and R. Steinmetz, Tetrahedron Letters, No. 21 (September), 1 (1960).

The product from toluene had m.p. 250-270°; this wide melting point range was attributed to the presence of isomers and two crystalline tetra-methyl esters of m.p. 105-107° and 163-165° have been isolated. The products from o-xylene and chlorobenzene are reported to have m.p. 280° (dec) and 260° (dec) respectively. These products are all described as non-aromatic on the basis of their spectroscopic properties. It is notable that Schenck and Steinmetz did not report any products formed from combination of one mole of maleic anhydride with one mole of aromatic compound as was found in the present work with toluene and p-xylene.

Experimental Details

Thiophene and Maleic Anhydride. -- A solution of 10 g. of maleic anhydride in 270 ml. of thiophene (b.p. 84.0-84.5°) was irradiated with ultraviolet light for 18 hours in the usual quantz apparatus (see Part I). The thiophene solution was extracted four times with in all 250 ml. of water to remove maleic anhydride. The thiophene layer after drying over anhydrous $MgSO_4$ was evaporated to dryness on a stream bath to give about 0.2 g. of a dark brown residue. The dark colored residue gave a strong positive test for sulfur upon sodium fusion. The residue was distilled at 0.03 mm. at a bath temperature up to 350° to give 0.09 g. of red-black tarry distillate. This distillate was soluble in aqueous KOH but almost insoluble in water. The potassium hydroxide solution of the distillate was extracted three times with ether (the ether extract contained a little spicy-smelling oil). Acidification of the solution, extraction with ether, and evaporation of the ether phase gave, after distillation at 0.03 mm. and a bath temperature up to 350°, 0.03 g. of red-black tar. This tar was insoluble in water, soluble in aqueous KOH, and gave a strong test for sulfur on sodium fusion. The walls of the quartz cell used in this irradiation were coated with some 0.3 g. of dark brown film which

gave a moderately strong test for sulfur upon sodium fusion. Only a small amount of the film dissolved in aqueous KOH (somewhat more than in water alone) and a little of the film melted near 110° but the remainder was not molten up to 348°.

Chlorobenzene and Maleic Anhydride. -- A solution of maleic anhydride (10 g.) in 330 ml. of chlorobenzene was irradiated with ultraviolet light for 20.3 hours in the usual quartz apparatus. Filtration of the reaction solution gave 0.28 g. of an orange colored solid (which was completely soluble in acetone) and washing the quartz apparatus with acetone gave 0.39 g. of acetone-soluble brown solid. An attempt to sublime or distill these combined solids at 0.04 mm. and a bath temperature up to 350° gave only 0.09 g. of semi-solid light brown distillate and a brown-black residue which was insoluble in acetone (obviously pyrolysis occurred). The chlorobenzene solution from the irradiation was washed four times with, in all, 250 ml. of water. Evaporation of the chlorobenzene at a bath temperature up to 200° gave 0.36 g. of dark red tar which was readily soluble in acetone. This tar gave a strong test for chlorine upon sodium fusion. The tar was nearly completely soluble in warm aqueous KOH although it was insoluble in water. The potassium hydroxide solution of the tar was treated with Nuclear C, filtered and then acidified to give a brown powder of m.p. near 125-143° with evolution of a gas near 185°.

Toluene and Maleic Anhydride. -- Irradiation experiments were run with 10.0 g. of maleic anhydride in about 320 ml. of thiophene-free toluene in the usual quartz apparatus with illumination with ultraviolet light for 20 to 25 hours. The toluene solution was extracted with four or five portions of water of about 60 ml. each to wash out unreacted maleic anhydride. The toluene was then evaporated at steam-bath temperature in vacuo to give a yellow oil.

In one such experiment 8.2 g. of semi-crystalline yellow oil was obtained. Recrystallization from acetone-n-hexane gave 0.85 g. of crystals of m.p. 143-152° which after further purification (including a vacuum sublimation at 158° and 0.015 mm. pressure) had m.p. 162-163°. These crystals gave the following analysis in agreement with that expected for benzylsuccinic acid (m.p. recorded[1] 161-162°).

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.53, 63.14; H, 5.68, 5.91.

Esterification of a portion of the remaining yellow oil with 1.4 N hydrogen chloride in methanol gave (after removal of the methanol and washing an ether solution of the product with aqueous $NaHCO_3$ to remove any unesterified acids) traces of crystals of m.p. 62-75° and an oil. The oil was distilled once at a bath temperature up to 190° and two more times with a bath temperature up to 150° at 0.02 mm. pressure. Gas chromatography of this oily methyl ester fraction on a column packed with finely pulverized fire brick impregnated with a silicone (Fisher-Gulf Partitioner Model 300) gave two strong, two medium, and four weak peaks with a retention time of about 45 minutes at 288° or 100 minutes at 248°.

In another run the pale yellow liquid product from the irradiation was hydrolyzed by heating at reflux for one hour with 2.5 N sodium hydroxide. There was isolated 5.0 g. of pale yellow syrupy acids from which by crystallization from chloroform and chromatography on a column packed with silicic acid with use of chloroform as an eluent there was isolated 67% by weight of benzylsuccinic acid (m.p. of various fractions 150-159°) with the remainder liquid or glassy product.

In another run 9.76 g. of liquid product was isolated from the irradiation. This was hydrolyzed by heating at reflux with aqueous alkali and an ether solution of the acid obtained in this manner was esterified by addition of diazomethane until a pale yellow color persisted. The ester, after removal of the ether was distilled at 0.15 mm. pressure at a bath temperature up to 160° to give 2.0 g. of a pale yellow liquid. A portion of this ester (1.0 g.) was saponified by heating at reflux for three hours with 100 ml. of 2.4 N potassium hydroxide. Acidification of this solution gave 0.9 g. of benzylsuccinic acid of m.p. 158-160°. Gas chromatography of the volatile methyl ester indicated the presence of only a single component.

In another irradiation conducted in the usual manner with the quantities of reagents specified above but with hydroquinone (< 1g.) before irradiation there was obtained only 3.5 g. of liquid adduct.

In a final irradiation experiment to 10 g. of maleic anhydride in 275 ml. of toluene was added 1.0 g. of hydroquinone dissolved in 50 ml. of acetone.

Through the resulting homogeneous solution nitrogen gas was bubbled throughout the 24 hour period of irradiation; there was obtained 1.39 g. of product. This product (after hydrolysis) contains at least 40% benzylsuccinic acid according to a separation by crystallization from chloroform.

p-Xylene and Maleic Anhydride. -- Freshly distilled maleic anhydride (10.0 g.) was dissolved in 300 ml. of p-xylene (thiophene-free grade) and the solution was irradiated with ultraviolet light for 23 hours in the usual quartz apparatus. The p-xylene solution was washed with five 60 ml. portions of water and then dried over anhydrous $MgSO_4$. The p-xylene was removed by distillation in vacuo at steam bath temperature to give 6.68 g. of oily solid. This product was crystallized from n-hexane to give 1.10 g. of crystals of m.p. 85-87° and 5.56 g. of oil. The crystalline product was recrystallized from n-hexane and sublimed at 0.015 mm. (bath temperature of 100°) to give a product of m.p. 86-87°.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 69.72, 70.49; H, 5.88, 6.07.

This crystalline substance has satisfactory analysis for p-methylbenzylsuccinic anhydride. Saponification of this substance gave an acid of m.p. 115-117.5° (recorded[2] m.p. for p-methylbenzylusuccinic acid 114-115°). The above 5.56 g. of oil was esterified by heating at reflux one hour with 200 ml. of methanol saturated with dry hydrogen chloride. The excess methanol was removed by distillation on a steam bath and the resulting liquid was taken up in ether. The ethereal solution was extracted several times with portions of aqueous sodium bicarbonate. The ether solution was dried over anhydrous $MgSO_4$ and distilled finally in vacuo at 0.05 mm. with a bath temperature up to 190°. There resulted 3.0 g. of a pale yellow liquid ester whose color was not removed by another distillation. A portion of the ester (1.0 g.) was saponified to give 0.8 g. of acid of m.p. 113.5-114.0°. Recrystallization from n-hexane gave a product of m.p. 115-117°. The oily product therefore appears to consist of at least 40% p-methylbenzylsuccinic anhydride.

Naphthalene and Maleic Anhydride. -- Naphthalene (67 g. or 0.52 mole) upon dissolving in 165 ml. of acetone containing 82 g. (0.84 mole) of freshly distilled maleic anhydride gave a yellow solution which was irradiated for

17.4 hours with ultraviolet light in the usual quartz apparatus. At the end of this time the light brown solution was evaporated on a steam bath to remove acetone and then worked up according to the procedure of Kloetzel and Herzog[5] for the one to one adducts of maleic anhydride with naphthalene and derivatives.

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(5) M. C. Kloetzel and H. L. Herzog, J. Am. Chem. Soc., 72, 1991 (1950).

There was recovered 65.5 g. (97.8% recovery) of unreacted naphthalene and a small amount of fumaric acid.

Part III

Photochemical Reaction of Dimethyl Acetylenedicarboxylate with Benzene

SUMMARY

Dimethyl acetylenedicarboxylate reacts with benzene at room temperature under irradiation by ultraviolet light to give, among other products, a substance which is provisionally assigned the structure of dimethyl cyclooctatetraene-1,2-dicarboxylate.

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Benzene with dimethyl acetylenedicarboxylate upon irradiation with ultraviolet light affords apparently a mixture of products from which a yellow crystalline compound of m.p. 109.4-110.4° has been isolated. This compound has a satisfactory analysis for an adduct from one mole of benzene combined with one mole of dimethyl acetylenedicarboxylate and, since the compound can be sublimed at a bath temperature of 102° at a pressure of 0.03 mm., has the molecular formula $C_{12}H_{12}O_4$. Saponification of the yellow methyl ester gives a yellow carboxylic acid of m.p. 206-208° (dec). This carboxylic acid has elementary analysis and volatility corresponding to the molecular formula $C_{10}H_8O_4$ as expected for an adduct from one mole of benzene combined with one mole of acetylenedicarboxylic acid. In agreement with the analytical data the adduct is tentatively assigned the structure of dimethyl cyclooctatetraene-1, 2-dicarboxylate.

This structural assignment is supported by comparisons of color and ultraviolet and infrared absorption spectra of our acid with that of previously reported cyclooctatetraene-monocarboxylic acid[1]. Upon hydrogenation in acetic acid over a 5% Pt on carbon catalyst, our yellow acid absorbed 2.95 moles of

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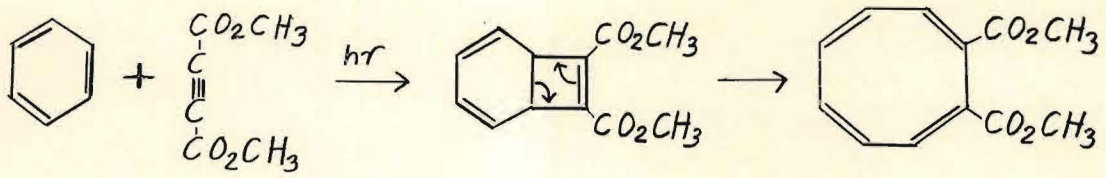
(1) A. C. Cope, M. Burg, and S. W. Fenton, J. Am. Chem. Soc., 74, 173 (1952).

hydrogen per mole of acid in 4 hours and 0.60 additional moles in 91 hours; again this behavior is similar to that reported for cycloöctatetraenemonocarboxylic acid[1].

It is postulated that dimethyl cycloöctatetraene-1,2-dicarboxylate is formed from benzene and dimethyl acetylenedicarboxylate by the following path:



Experimental Details

Irradiation of Dimethyl Acetylenedicarboxylate in Benzene. -- Dimethyl acetylenedicarboxylate (20 ml. of b.p. 96-97° at 20 mm.) was dissolved in 300 ml. of thiophene-free benzene and the solution was irradiated for 24 hours in the usual quartz apparatus (see Part I). The benzene and unreacted dimethyl acetylenedicarboxylate (some 14 g. recoverable) were removed in vacuo with heat supplied as required by a steam bath. The residue was distilled in a sublimation apparatus and 0.7 to 0.8 g. of yellow crystals were deposited on the condenser at a pressure of 0.10 to 0.03 mm. and a bath temperature of 95 to 151°. A dark red glassy residue remained undistilled. This residue is soluble in benzene and in acetone, but has not been further investigated. The yellow crystals were combined with about an equal amount of crystals from a similar run and upon resublimation at 102° at 0.03 mm. gave 1.4 g. of crystals of m.p. 107.2-108.6°. After two recrystallizations from methanol crystals of m.p. 109.2-110.4° were obtained. The sample for analysis was sublimed again to give 0.8 g. of crystals of m.p. 109.4-110.4°.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.43; H, 5.49; saponification equiv., 110.1. Found: C, 65.19, 65.39; H, 5.11, 5.35; saponification equiv., 107, 103.

Saponification of the Ester. -- The ester (1.0 g.) of m.p. 109.4-110.4° from benzene and dimethyl acetylenedicarboxylate was dissolved in 25 ml. of

95% ethanol containing 1.2 g. of potassium hydroxide and the solution heated at reflux for two hours. A crystalline solid separated from the solution during this time. The solvent was removed in vacuo and the residual potassium salt was acidified with 6 N hydrochloric acid. A pale yellow crystalline solid (0.9 g.) of m.p. 202-203° (dec.) precipitated. The product was recrystallized from hot water. A sample for analysis was sublimed at a bath temperature of 173-210° and a pressure of 0.94 mm. to give a product of m.p. 206.5-208° (dec). This sample was recrystallized from water and resublimed before analysis.

Anal. Calcd. for $C_{10}H_8O_4$: C, 62.50; H, 4.20. Found: C, 62.15, 62.34; H, 4.08, 4.18.

Respectfully submitted,

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